Bond-Length Change as a Tool to Determine Charge Transfer and Electron-Phonon Coupling in Graphite Intercalation Compounds

L. Pietronero and S. Strässler
Brown Boveri Research Center, CH-5405 Baden, Switzerland

(Received 11 March 1981)

A theory is formulated that explains the observed bond-length change in graphite intercalation compounds in terms of the charge transfer f. The values of f obtained via the bond-length changes are in good agreement with those derived with other methods. The present analysis also provides information on the electron-phonon coupling that defines the maximum conductivity.

PACS numbers: 61.10.-i, 62.20.-x, 71.90.+q

To understand most of the properties of graphite intercalation compounds one first has to determine the charge transfer and the electron-phonon coupling. These two quantities are essential for the calculation of the maximum conductivity of these systems.[1]

The purpose of this Letter is to show how the value of the charge transfer and information about the electron-phonon coupling can be extracted from the changes in carbon-carbon bond length upon intercalation. One advantage of this method is in the availability of several high-precision measurements of the bond-length change as in the cases of graphite intercalation compounds with Li,[2] K,[3] and Cs [3] (see Fig. 1). Also, with respect to the theory, we can start from the methods that have been used successfully to explain the bond-length changes in carbon-based molecules[7-10] and extend them to intercalated graphite.

Following Kakitani[8] and using the tight-binding method[13] we can write the total energy per bond between nearest-neighboring atoms at points n and n' as

$$E_{n,n'}{}^{T} = E_{n,n'}{}^{\sigma} + E_{n,n'}{}^{\pi}, \tag{1}$$

where E^σ and E^π are the energies of the σ and π electrons, respectively. Neglecting the terms that do not depend on bond length we can write

$$E_{n,n'}{}^{\pi} = 2P_{n,n'}J_{n,n'}{}^{pp\pi}, \tag{2}$$

where

$$J_{n,n'}{}^{pp\pi} = \langle p_n{}^z \,|\, V_n \,|\, p_{n'}{}^z\rangle \tag{3}$$

(z indicates the direction perpendicular to the layer) is the (off-diagonal) tight-binding matrix element between p^z orbitals of nearest-neighboring atoms[10] at position n and n' and V_n is an effective atomic potential. Crystal-field (diagonal) terms are not included (see later discussion). $P_{n,n'}$ is the bond order for π electrons defined as[9]

$$P_{n,n'} = 2 \sum_{\vec{k}\,(\text{occupied})} c_n{}^*(\vec{k})c_{n'}(\vec{k}), \tag{4}$$

where $c_n(\vec{k})$ is the coefficient of the p^z orbital at point n corresponding to the state $\vec{k}$. Since we are only interested in uniform contractions or expansion we can omit the indices n and n'. It is important to notice that systems with exactly the

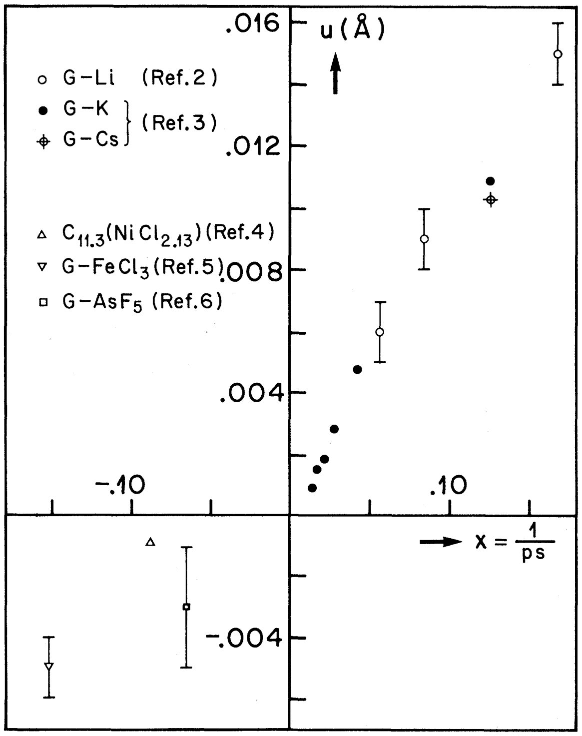

FIG. 1. Experimental values for the bond-length change $u = r - r_0$ ($r_0 = 1.421$ Å) for various intercalation compounds plotted as a function of the ratio of the number of intercalate molecules to the number of carbon atoms in a given compound. The nominal formula of a compound is CA_x, where $x = 1/ps$, s is the stage, and $p = 6$, 8, etc.

same charge on the p^z orbitals (one electron per atom) but different geometries, such as ethylene, benzene, polyacetylene (without bond alternation), and a neutral graphite layer, have very different values of the bond order. These values are, respectively, 1,[8] $\frac{2}{3}$,[8] $2/\pi$,[7] and 0.525.[11]

The σ band is described in terms of bonding states between sp_2 hybrids.[9] This gives rise to[12] (apart from constant terms)

$$E^{\sigma}(r)=\tfrac{2}{3}J^{ss\sigma}(r)-\tfrac{4}{3}J^{pp\sigma}(r), \tag{5}$$

where, as in Ref. 13,

$$\begin{aligned} J^{ss\sigma}(r)&=\langle s_n\,|\,V_n\,|\,s_{n'}\rangle,\\ J^{pp\sigma}(r)&=\langle p_n{}^x\,|\,V_n\,|p_{n'}{}^x\rangle, \end{aligned} \tag{6}$$

and r is the bond length.

Let us consider for the moment a single layer charged with an electronic charge f_c per carbon atom. This extra charge gives rise to the following effects: (a) A modification of the occupancy of the π states that changes the value of the bond order: $P=P_0+\Delta P(f_c)$, where $P_0=0.525$ is the value for the neutral layer. (b) A modification of all the matrix elements due to the fact that the atomic potential is changed: $J=J_0+\Delta J(f_c)$. (c) In addition, since the layers acquire a net charge we also estimate the contribution $\Delta E_{\rm el}$ (also defined per bond) to the total energy due to the Coulomb repulsion between the charged atoms. This effect is linked microscopically to crystal-field terms and as we will see it is quite small.

$$E^T(f_c;r)=2[P_0+\Delta P(f_c)][J_0{}^{pp\pi}(r)+\Delta J^{pp\pi}(f_c;r)]+\tfrac{2}{3}[J_0{}^{ss\sigma}(r)+\Delta J^{ss\sigma}(f_c;r)]-\tfrac{4}{3}[J_0{}^{pp\sigma}(r)+\Delta J^{pp\sigma}(f_c;r)]+\Delta E_{\rm el}(f_c;r). \tag{7}$$

We now write $r=r_0+u$, where $r_0=1.421$ Å is the equilibrium bond length for the neutral layer ($f_c=0$). We then expand Eq. (7) up to quadratic terms in u making use of the condition that r_0 is the equilibrium position for $f_c=0$. The equilibrium condition for the general case now gives the displacement u as (neglecting the terms $\Delta P\Delta J$, $\Delta J\Delta J$, and $\Delta P\Delta P$)

$$u=-\frac{1}{K}\left(2\Delta P(f_c)\frac{dJ_0{}^{pp\pi}(r)}{dr}\bigg|_{r_0}+2P_0\frac{d\Delta J^{pp\pi}(r)}{dr}\bigg|_{r_0}+\frac{d\Delta E^{\sigma}(f_c;r)}{dr}\bigg|_{r_0}+\frac{d\Delta E_{\rm el}(f_c;r)}{dr}\bigg|_{r_0}\right), \tag{8}$$

where

$$\Delta E^{\sigma}(f_c;r)=\tfrac{2}{3}\Delta J^{ss\sigma}(f_c;r)-\tfrac{4}{3}\Delta J^{pp\sigma}(f_c;r), \tag{9}$$

and

$$K=\frac{d^2E^T(f_c=0;r)}{dr^2}\bigg|_{r_0} \tag{10}$$

is the total bond-stretching force constant of neutral graphite. Note that since we retain only terms linear in ΔP or ΔJ there is no problem of double counting with respect to electron-electron repulsion. This problem would appear in terms like $\Delta P\Delta J$, $\Delta J\Delta J$, and $\Delta P\Delta P$ that are neglected here. In addition crystal-field–type terms are only included phenomenologically in $\Delta E_{\rm el}$ because their eventual linear contribution would only be of local-field type.

As one can see from Fig. 1 graphite expands if electrons are added (donors) and shrinks if they are subtracted (acceptors).[14] The opposite seems to happen in small molecules because the bond lengths of ethane (single bond), benzene (alternating single and double bond), and ethylene (double bond) are, respectively,[8] 1.536, 1.397, and 1.337 Å. The main difference between intercalated graphite and the molecules is that in the first case a net charge appears on the carbon atoms while in the second case the carbon atoms are neutral and only the bond order is changed.

We now evaluate the various terms that appear in Eq. (8). The total force constant K can be computed both from the elastic constants of graphite[15] and from the analysis of small molecules extrapolated to the bond length of graphite.[8] Both of these methods give $K=45$ eV/Å^2. For the evaluation of the matrix elements J and ΔJ and their derivatives we use Slater orbitals for the wave functions with the exponent optimized for the carbon atom[16] ($\xi=1.59$ in atomic units). The potential is constructed as the electrostatic potential corresponding to these orbitals but with use of a different exponent ($\xi'=1.27$) in order to obtain $J_0{}^{pp\pi}(r_0)=2.4$ eV.[10,17] This gives $dJ^{pp\pi}/dr|_{r_0}=6.3$ eV/Å which is also the value we have used in the calculation of conductivity.[1,10] This value is in agreement with the observed gap of polyacetylene and the analysis of its Raman modes,[12] but it is about 25% larger than the value obtained by Kakitani from small molecules.[8] For the matrix elements of type ΔJ we consider a ΔV due to the charge transfer from intercalate molecules to spherically averaged p^z orbitals. The charge on the intercalate molecules is replaced by a uniform (compensating) surface charge on a sphere of radius $R = 3$ Å.[12] The results are not very sensitive to the specific model chosen for the neutralizing charge as the main contribution comes from the extra charge on the carbon atoms. We obtain then

$$\left.\frac{d\Delta J^{pp\pi}(r)}{dr}\right|_{r_0} = -3.34 f_c\ \mathrm{eV/\AA},$$
$$\left.\frac{d\Delta J^{ss\sigma}(r)}{dr}\right|_{r_0} = -4.51 f_c\ \mathrm{eV/\AA}, \qquad (11)$$
$$\left.\frac{d\Delta J^{pp\sigma}(r)}{dr}\right|_{r_0} = 0.43 f_c\ \mathrm{eV/\AA}.$$

The change in bond order within the linear band approximation is given by[12] (corrections due to nonlinearity decrease the value of P by about 10% for LiC_6 and much less for other compounds[12])

$$\Delta P(f_c) = \frac{\Delta E^{\pi}(f_c)}{2J_0^{pp\pi}(r_0)} = -2\cdot 3^{-7/4}\sqrt{\pi}\,|f_c|^{3/2}$$
$$= -0.52|f_c|^{3/2}. \qquad (12)$$

To estimate the last term in Eq. (8) we consider the electrostatic energy of a uniform charge density within the volume of a graphite layer,[18]

$$\left.\frac{d\Delta E_{\mathrm{el}}(f_c;r)}{dr}\right|_{r_0} = -\frac{32\pi}{27\sqrt{3}}\,\frac{e^2 c}{\epsilon_\perp r_0^3} f_c^2$$
$$= -10.60 f_c^2\ \mathrm{eV/\AA}, \qquad (13)$$

where $\epsilon_\perp \simeq 3.4$ (Ref. 19) is the dielectric constant and $c = 3.35$ Å is the layer thickness. Since $f_c \leq \frac{1}{6}$, this term is always small. Besides this quadratic term crystal-field effects also produce a linear term in f_c as a result of the interaction of the extra charge with the neutral carbon potential. With our parameters we find that for $f_c \gtrsim 0.01$ the quadratic term already dominates. We neglect therefore this extra linear term.

The final result for state 1 is then

$$u(1)\ (\mathrm{\AA}) = 0.157 f_c + 0.146|f_c|^{3/2} + 0.236 f_c^2. \qquad (14)$$

Note that since $f_c \leq \frac{1}{6}$ the leading term is the linear one that is due to effects that are *beyond the rigid-bond model.* It is this contribution that results in the interesting physical effect of the bond expanding for donors and shrinking for acceptors. The deviations from linearity in Eq. (14) are then mainly due to the second term whose coefficient is directly related to $dJ^{pp\pi}/dr$ and therefore to the electron-phonon coupling that defines the maximum ideal conductivity of these systems.[1] In order to generalize this result to higher stages we assume (i) that the charge is localized in the bounding layers[17] (f_c only refers to these) and (ii) that the strain is equally shared by all the layers. Note that assumption (i) is not strictly valid[18] but for total energy considerations is acceptable. We obtain then

$$u(s) = (2/s)u(1), \quad s \geq 2. \qquad (15)$$

TABLE I. Values of the charge transfer per intercalate molecule obtained from the analysis of the data of Fig. 1 through Eqs. (14) and (15) compared with the values given from other experiments. Note that in our model the charge transfer refers to the filling of the graphite π bonds. This does not necessarily coincide with the ionization of the intercalate; therefore caution must be taken in comparing the charge transfer obtained with different methods.

	f (previous methods)	f (present analysis)
C_6Li	0.22–0.42 [a]	0.43
	~1 [b]	
$C_{12}Li$		0.54
$C_{18}Li$		0.55
C_8K	0.16–0.45 [a]	0.43
	~0.3 [c]	
$C_{24}K$	~1 [a]	0.63
$C_{36}K$	0.1–0.4[d]	0.57
$C_{48}K$		0.50
C_8Cs	0.17–0.44 [a]	0.41
	~0.3 [c]	
	0.5 ± 0.2 [e]	
$C_{16}AsF_5$	– (0.26–0.44) [a]	~ – 0.35
	– 0.48 [f]	
	– 0.41 [g]	
	– (0.4–0.5) [h]	
	– (0.30–0.51) [i]	
	– 0.22 [j]	
$C_{6.6}FeCl_3$	– 0.18 [k]	– 0.26
$C_{11.3}NiCl_{2.13}$		– 0.07

[a] Ref. 20.
[b] Ref. 21.
[c] Ref. 22.
[d] Ref. 23.
[e] Ref. 24.
[f] Ref. 25.
[g] Ref. 26.
[h] Ref. 27.
[i] Ref. 17.
[j] Ref. 28.
[k] Ref. 29.

In Fig. 1 we have plotted the available data for u as functions of $x = 1/ps$, where $p = 6$, 8, etc. The roughly linear behavior observed for groups of donors for $s \geq 2$ indicates that f_c is about constant. If the stage-1 compounds would also lay on this line (they are actually lower), because of the fact that the main term in Eq. (14) is the linear one, this would imply that f is also compound independent for stage 1. By f we mean the charge transferred into the graphite π bands per intercalate molecule. This does not necessarily coincide with the ionization of the intercalate.

In view of the availability of several values of u determined with high precision we have used the measured u's in Eqs. (14) and (15) to determine f_c and then f. The results are listed in Table I together with values of f determined with the other available methods. The overall excellent consistency of the present analysis provides strong support for the general picture we have been describing. In addition to supplying a new method for the determination of f it also validates the approach previously used to compute the conductivity.[1,10]

The authors are grateful to Professor J. Conard and Professor A. Hérold and to Dr. H. Estrade for interesting discussions and correspondence. They are also grateful to Dr. S. Flandrois and Dr. R. S. Markiewicz for communication of their results prior to publication.

---

[1] L. Pietronero and S. Strässler, Synthet. Metal 3, 209 (1981).

[2] D. Guérard, C. Zeller, and A. Hérold, C. R. Acad. Sci., Ser. C 283, 437 (1976).

[3] D. E. Nixon and G. S. Parry, J. Phys. C 2, 1732 (1969).

[4] S. Flandrois, J. M. Masson, J. C. Rouillon, J. Gaultier, and C. Hauw, to be published.

[5] A. Hérold, private communication.

[6] R. S. Markiewicz, J. C. Kasper, and L. V. Interrante, to be published.

[7] H. C. Longuet-Higgins and L. Salem, Proc. Roy. Soc. London, Ser. A 251, 172 (1959).

[8] T. Kakitani, Prog. Theor. Phys. 51, 656 (1974).

[9] J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules* (Chapman and Hall, London, 1971).

[10] L. Pietronero, S. Strässler, H. R. Zeller, and M. J. Rice, Phys. Rev. B 22, 904 (1980).

[11] C. A. Coulson and R. Taylor, Proc. Phys. Soc. London, Sect. A 65, 815 (1952).

[12] L. Pietronero and S. Strässler, to be published.

[13] F. Bassani and G. Pastori Parravicini, Nuovo Cimento B50, 4259 (1967), and *Electronic States and Optical Transitions in Solids* (Pergamon, Oxford, 1975).

[14] This behavior is also reflected in the shifts of phonon frequencies: M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. 30, 139 (1981).

[15] A. P. P. Nicholson and D. J. Bacon, J. Phys. C 10, 2295 (1977).

[16] H. F. Schaefer, III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, Mass., 1972).

[17] J. Blinowski, Nguyen Hy Hau, C. Rigaux, J. P. Vieren, R. Le Toullec, G. Furdin, A. Hérold, and J. Melin, J. Phys. (Paris) 41, 47 (1980).

[18] L. Pietronero, S. Strässler, H. R. Zeller, and M. J. Rice, Phys. Rev. Lett. 41, 763 (1978); L. Pietronero, S. Strässler, and H. R. Zeller, Solid State Commun. 30, 399 (1979).

[19] M. Zanini, D. Grubisic, and J. E. Fischer, Phys. Status Solidi (b) 90, 151 (1978).

[20] J. Conard, M. Gutierrez-Le Brun, P. Lauginie, H. Estrade-Szwarckopf, and G. Herman, to be published. A preliminary analysis that gives larger values for f can be found in J. Conard, H. Estrade, P. Lauginie, H. Fuzellier, G. Furdin, and R. Vasse, Physica (Utrecht) 99B, 521 (1980).

[21] W. Eberhardt, I. T. McGovern, E. W. Plummer, and J. E. Fischer, Phys. Rev. Lett. 44, 200 (1980).

[22] P. Oelhafen, P. Pfluger, E. Hauser, and H. J. Güntherodt, Phys. Rev. Lett. 44, 197 (1980).

[23] H. Suematsu, K. Higuchi, and S. Tanuma, J. Phys. Soc. Jpn. 48, 1541 (1980).

[24] L. E. Campbell, G. L. Monet, and G. J. Perlow, Phys. Rev. B 15, 3318 (1977).

[25] B. R. Weinberger, J. Kaufer, A. J. Heeger, J. E. Fischer, M. Moran, and N. A. W. Holzwarth, Phys. Rev. Lett. 41, 1417 (1978).

[26] R. S. Markiewicz, H. R. Hart, Jr., L. V. Interrante, and J. S. Kasper, to be published.

[27] J. J. Ritsko and E. J. Mele, to be published.

[28] Y. Iye, O. Takahashi, and S. Tanuma, Solid State Commun. 33, 1071 (1980).

[29] E. J. Mele and J. J. Ritsko, to be published.