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PHONON DISPERSION RELATIONS OF GRAPHITE AND FIRST STAGE ALKALI METAL–GRAPHITE INTERCALATION COMPOUNDS

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Summary

The phonon dispersion relations of graphite and first stage alkali metal–graphite intercalation compounds (KC_8) have been calculated using an angular force model approach. Initially, for graphite, the investigations were made by considering the interactions up to two neighbours in the plane and one neighbour between the planes. We present the first calculation of the phonon dispersion relations of graphite where the recent experimental measurement A_{2u} out of plane mode at 868 cm^{-1} is satisfactorily explained as output data, whereas earlier workers have presented the phonon spectrum considering this mode as input data. We have extended the analysis to the evaluation of the phonon spectrum and elastic constants of first stage potassium–graphite intercalation compounds. Good agreement has been observed between theory and the available experimental results. An inference is drawn that the angular forces play a vital role in explaining the acoustic modes of the phonon spectra.

Introduction

Graphite intercalation compounds have been the focus of a considerable amount of theoretical and experimental research activity during the past decade [1 - 10]. Graphite intercalation compounds are formed by introducing the intercalate between the carbon layers of graphite. Such a process results in the ordering of the c-axis, known as the staging phenomenon. There are n consecutive graphite layers followed by an intercalate layer for a stage n graphite intercalation compound.

Experimental phonon dispersion curves are now available through neutron and Raman scattering experiments for $(00q)$ longitudinal phonons in the case of alkali metal–graphite intercalation compounds [9, 10]. Lattice dynamic calculations for GICs have been very few. The first calculation for the first stage alkali–GICs was reported by Horie *et al.* [4] based on the Maeda model [11] for the lattice dynamics of pristine graphite. Leung *et al.* [5] evaluated the dispersion curves for all GIC stages from those of pristine graphite by carrying out a k_z axis zone folding of the graphite dynamical

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matrix and replacing the appropriate carbon layers with intercalate layers. Recently Al-Jishi and Dresselhaus [7] have extended Leung's approach, incorporating all the experimental information. In these calculations the phonon dispersion curves for alkali metal–GICs have been investigated by fitting the various force constants to the experimentally measured phonon frequencies, causing the model to be biased towards the experimental phonon spectra.

In our case we have used the de Launey [12] type angular force model approach to study initially the phonon dispersion curves of graphite. The central force constants α_1, α_2, and α_3 are operative for two neighbours in the plane and one neighbour between the planes, respectively, whereas the angular force constants α_1', α_3' have been considered only up to the first neghbour in the plane and the first neighbour between the planes. The five force constants were then reduced to four by taking the relation $\alpha_1 = 5\alpha_1'$. This is validated by the fact that the numerical value of α_1' will be less than α_1 by an order of magnitude in the range of the square of the interatomic spacing [13]. These four force constants were then evaluated by fitting to three elastic constants and one experimental frequency only. Using these four force constants, we have been able to exhibit for the first time the A_{2u} out of plane mode at 868 cm^{-1} satisfactorily.

The above model for graphite has been extended to calculate the phonon dispersion of stage I potassium–GIC, KC_8. The stacking sequence has been considered to be of the type $C\alpha C\alpha C\alpha C\alpha$ where C represents the carbon layer and α the intercalate layer. We have incorporated the C–K interlayer interactions (β_1, β_1') as used by Horie *et al.* [4]. The interlayer interaction C–C has been taken from the above mentioned graphite calculations. The sum and difference modes analysis [14] has been used for the evaluation of the eighteen phonon frequencies of KC_8. The use of the sum and difference mode was possible because the carbon layers have the same structure in GICs. The phonon dispersion and the elastic constants of KC_8 have been analysed and very good agreement has been obtained with the available experimental results [9, 10].

Theory

The dynamical matrix elements have been obtained on the lines of de Launey [12]. The sum and difference mode analysis [14] interprets the vibrational spectra from the following dynamical matrices:

For graphite:

$$\begin{vmatrix} A \pm T - m_c\omega^2 & B \pm D \\ B^* \pm D^* & A \pm T - m_c\omega^2 \end{vmatrix} = 0 \qquad (1)$$

where A, B, D and T are 3×3 matrices with elements derived as follows:

$$A_{11} = P + 3\alpha_2(1 - CC') + 2\alpha_3'$$

$$A_{12} = A_{21} = \sqrt{3}\alpha_2 SS'$$

$$A_{22} = P + \alpha_2(3 - 2C'' - CC') + 2\alpha_3'$$

$$A_{33} = 3\alpha_1' + 2\alpha_3'$$

$$B_{11} = -\alpha_1'[Q + 2RC'] - (\alpha_1 - \alpha_1')[Q + \tfrac{1}{2}RC']$$

$$B_{12} = B_{21} = \sqrt{3}i/2(\alpha_1 - \alpha_1')RS'$$

$$B_{22} = -\alpha_1'[Q + 2RC'] - 3/2(\alpha_1 - \alpha_1')RC'$$

$$B_{33} = -\alpha_1'[2RC' + Q]$$

$$T_{11} = T_{22} = -2\alpha_3'C'''$$

$$T_{33} = -2\alpha_3 C'''$$

$$A_{13} = A_{31} = A_{23} = A_{32} = 0$$

$$B_{13} = B_{31} = B_{23} = B_{32} = 0$$

$$D_{13} = D_{12} = D_{31} = D_{21} = D_{23} = D_{32} = D_{11} = D_{22} = D_{33} = 0$$

$$T_{12} = T_{21} = T_{13} = T_{31} = T_{23} = T_{32} = 0$$

For KC_8 it will be:

$$\begin{vmatrix} E \pm F - m_c\omega^2 & G \pm H & I \pm J \\ G^* \pm H^* & K \pm F - m_c\omega^2 & L \pm M \\ I^* \pm J^* & L^* \pm M^* & N \pm u - m_k\omega^2 \end{vmatrix} = 0 \qquad (2)$$

where E, F, G, H, I, J, K, L, M, N, u are 3×3 matrices with elements given by:

$$E_{11} = P + 3\alpha_2(1 - CC') + 2\alpha_3' + 2\beta_1'$$

$$E_{12} = E_{21} = \sqrt{3}\alpha_2 SS'$$

$$E_{22} = P + \alpha_2(3 - 2C'' - CC') + 2\alpha_3' + 2\beta_1'$$

$$E_{33} = 3\alpha_1' + 2\alpha_3 + 2\beta_1$$

$$G_{11} = -\alpha_1'[Q + 2RC'] - (\alpha_1 - \alpha_1')[Q + \tfrac{1}{2}RC']$$

$$G_{12} = G_{21} = \sqrt{3}i/2(\alpha_1 - \alpha_1')RS'$$

$$G_{22} = -\alpha_1'[Q + 2RC'] - 3/2(\alpha_1 - \alpha_1')RC'$$

$$G_{33} = -\alpha_1'[Q + 2RC']$$

$$I_{11} = I_{22} = -2\beta_1' C''''$$

$$I_{33} = -2\beta_1 C''''$$

$$K_{11} = P + 3\alpha_2(1 - CC') + 2\alpha_3'$$

$$K_{12} = K_{21} = \sqrt{3}\alpha_2 SS'$$

$$K_{22} = P + \alpha_2(3 - CC' - 2C'') + 2\alpha_3'$$

$$K_{33} = 3\alpha_1' + 2\alpha_3$$

$$N_{11} = N_{22} = 2\beta_1'$$

$$N_{33} = 2\beta_1$$

$$F_{11} = F_{22} = -2\alpha_3' C'''$$

$$F_{33} = -2\alpha_3 C'''$$

$$E_{13} = E_{31} = E_{23} = E_{32} = G_{13} = G_{31} = G_{23} = G_{32} = 0$$

$$I_{12} = I_{21} = I_{13} = I_{31} = I_{23} = I_{32} = 0$$

$$K_{13} = K_{31} = K_{23} = K_{32} = N_{12} = N_{21} = N_{13} = N_{31} = N_{23} = N_{32} = 0$$

$$L_{11} = L_{22} = L_{33} = L_{12} = L_{21} = L_{13} = L_{31} = L_{23} = L_{32} = 0$$

$$F_{12} = F_{21} = F_{13} = F_{31} = F_{23} = F_{32} = H_{11} = H_{22} = H_{33} = H_{12} = H_{21} = 0$$

$$H_{13} = H_{31} = H_{23} = H_{32} = J_{11} = J_{22} = J_{33} = J_{12} = J_{21} = J_{13} = J_{31} = 0$$

$$J_{23} = J_{32} = M_{11} = M_{22} = M_{33} = M_{12} = M_{21} = M_{13} = M_{31} = M_{32} = 0$$

$$u_{11} = u_{22} = u_{33} = u_{12} = u_{21} = u_{13} = u_{31} = u_{23} = u_{32} = 0$$

with

$$C = \cos(\pi\sqrt{3}aK_1), \qquad C' = \cos(\pi aK_2), \qquad C'' = \cos(2\pi aK_2)$$

$$C''' = \cos(\pi K_3 c), \qquad C'''' = \cos(\pi K_3 c/2)$$

$$S = \sin(\pi\sqrt{3}aK_1), \qquad S' = \sin(\pi aK_2), \qquad S'' = \sin(2\pi aK_2)$$

and

$$P = 3/2(\alpha_1 + \alpha_1'), \qquad Q = \exp(2\pi aiK_1/\sqrt{3})$$

$$R = \exp(-\pi aiK_1/\sqrt{3})$$

Results and discussion

Using the force constants shown in Table 1, the frequencies have been calculated in the (q00), (0q0) and (00q) directions for graphite and KC_8. They are shown in Figs. 1 and 2, respectively, wherein our results have been compared with the experimental results of Nicklow *et al.* [15] in Fig. 1, and with those of Zabel *et al.* [9, 10] in Fig. 2. Excellent agreement may be seen

TABLE 1

Value of force constants

Force constant	α_1	α_1'	α_2	α_3	α_3'	β_1	β_1'
Value in units of 10^4 D/cm	49.055	9.811	5.642	0.300	0.033	1.000 [4]	0.100 [4]

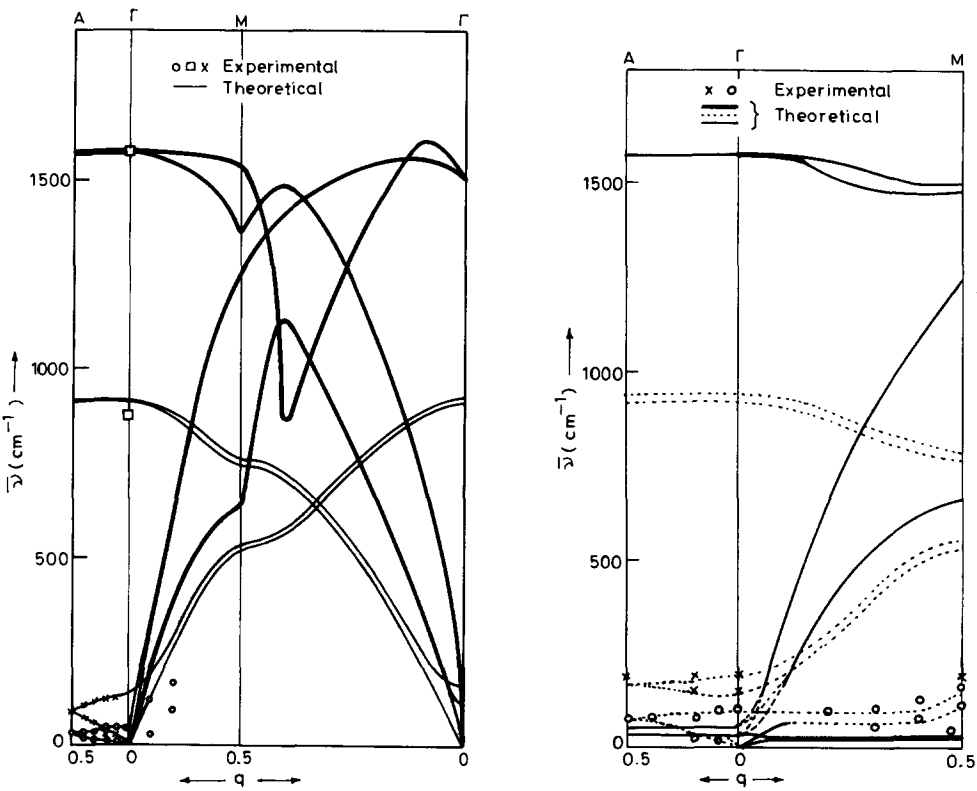

Fig. 1. Phonon dispersion in graphite. A heavy line indicates a doublet (two lines merged into one because of the present scale).

Fig. 2. Phonon dispersion in first stage potassium–graphite intercalation compound. ▬▬, a quartet; ——, a doublet; ·····, a single line.

in each of the Figures, especially in the acoustical branches. For graphite, however, there is a slight deviation in the $TA_{\perp}$ branch in the $(q00)$ direction. The curve exhibits linear behaviour at low wave vectors, whereas the experimental points lie on a quadratic curve. This is attributed to the exclusion of α_2', the angular force constant for the second neighbour interaction. However, the present analysis shows the A_{2u} out of plane mode at 868 cm^{-1} to be suitable as output data, a result not explained earlier.

In the case of KC_8 we have been able to obtain very good agreement in the cases of the acoustical branches in the $(00q)$ and $(q00)$ directions. Even for optical branches, wherever the measurements are available, the agreement is fair. If we compare our theoretical values with those of Al-Jishi [7] and Horie *et al.* [4], we find that our calculated modes are similar to those obtained by the workers in question.

Table 2 gives the calculated value of the elastic constants C_{44} and C_{33} along with the available experimental values [9, 10]. Very good agreement has been obtained in the case of C_{44}. For C_{33}, a comparison has been made with the values of Zabel *et al.* [9], where the agreement is not very satisfactory. It should be mentioned that the C_{33} values of Zabel *et al.* were obtained from the initial slope of the (001) LA branch and not measured directly.

TABLE 2

Value of elastic constants

Elastic constant	C_{44}	C_{33}
Value obtained in present case in units of 10^{11} D/cm^2	0.292	2.772
Experimental value in units of 10^{11} D/cm^2	0.282 [10]	4.850 [9]

Conclusion

The general conclusion that can be drawn from the discussion is that in explaining the vibrational spectra, the non-central force constants play a vital role. Secondly, the present approach can provide a basis for further study of the higher stage graphite–alkali metal intercalation compounds.

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