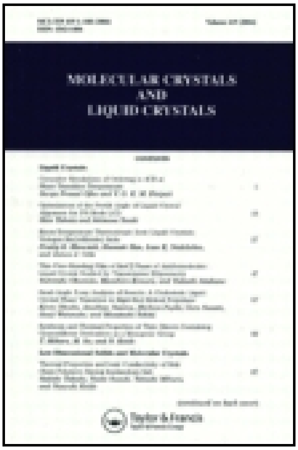

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2D Characterization of GICs

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2D CHARACTERIZATION OF GICs

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Abstract : using a dynamical model based on the De Launay method we evaluate the phonon dispersion curves and the density of states of a family of compounds including MC_6 compounds (M=Li, Ba, Ca, Sr, Sm, Eu, Yb) and MC_8 compounds (M=K, Rb, Cs). Using a power law to fit the specific heat of each compound we evaluate the 2 dimensionnal character of these compounds.

INTRODUCTION

Macroscopically graphite displays a layered appearance. This is due to the presence of planes with high atomic density and very weak interplanar interactions [1, 2, 3]. Graphite and graphite intercalation compounds (GICs) studies of phonon dispersions have been carried out but the models proposed need a great number of fitting parameters and are not used to estimate physical properties.

Our model is very simple : only five parameters for graphite and seven for graphite intercalation compounds. With those force constants we evaluate the density of states $g(\nu)$ of each compound which enables us to calculate the specific heat of the series. By fitting the exponential development of the specific heat for low (less than 160K) temperature we obtain the 2D character of the compounds.

STRUCTURE

In graphite, carbon atoms are localized at the corners of "open" hexagons. The inplane carbon-carbon distance is d_{cc}=1.420 Å[1, 2, 3]. Graphite can exhibit a rhombohedral structure, but this form is unstable and always poorly cristallized. Our study is limited to the hexagonal graphite with a stacking sequence $\mathcal{AB}$...; each $\mathcal{B}$ layer is obtained from an $\mathcal{A}$ layer by a double translation :

- a translation along the $\vec{c}$ axis $d_{pp} = 3.35$ Å, the interplanar distance.
- a translation $\vec{\tau}$ of length equal to $d_{cc} = 1.42$ Å

The other compounds studied here present also an hexagonal stucture but two successive planes are superposable. The parameters of the compounds are shown in table 1.

Table 1 : Parameters of the compounds[4, 5]

Compound	Stacking	d_{cc}(Å)	d_{pp}(Å)
Graphite	$ABAB$	1.420	3.35
LiC_6	$A\alpha$	1.435	3.706
CaC_6	$A\alpha A\beta$	1.43	4.60
SrC_6	$A\alpha A\beta$	1.439	4.94
BaC_6	$A\alpha A\beta$	1.434	5.25
EuC_6	$A\alpha A\beta$	1.438	4.58
SmC_6	$A\alpha A\beta$	1.437	4.87
YbC_6	$A\alpha A\beta$	1.440	4.57
KC_8	$A\alpha A\beta A\gamma A\delta$	1.432	5.32
RbC_8	$A\alpha A\beta A\gamma A\delta$	1.431	5.618
CsC_8	$A\alpha A\beta A\gamma$	1.431	5.928

THE DYNAMICAL MATRIX

To calculate the dynamical matrix of each compound we use a model based on the De Launay method[6].

De Launay's model [6]

The model postulates two types of atomic interactions :

- central forces : this kind depends only on the distance between two atoms;
- angular forces which are function of the angle between the equilibrium line joining two atoms and the line joining the atoms in their equilibrium positions.

The net force, called non-central force, is the sum of the central and the angular components. Equations of motion in the crystal are :

$$m_s \frac{d^2 u_{0si}}{dt^2} = \sum_{n's'\mu} \left(\overrightarrow{F_{0sn's'\mu}} \right)_i = -m_s \omega_{si}^2 u_{0si} \tag{1}$$

with

$$\overrightarrow{F_{0sn's'\mu}} = -\alpha'_\mu \left(\overrightarrow{u_{0s}} - \overrightarrow{u_{n's'}} \right) - (\alpha_\mu - \alpha'_\mu) \left[\overrightarrow{\epsilon_{n'}} . \left(\overrightarrow{u_{0s}} - \overrightarrow{u_{n's'}} \right) \overrightarrow{\epsilon_{n'}} \right] \tag{2}$$

μ is the order of the neighbourhood (first neighbours μ=1, second neighbours μ=2, ...). The eigensystem :

$$\left| D(\overrightarrow{k}) - m_s \omega_s^2(\overrightarrow{k}) I \right| = 0 \tag{3}$$

is equivalent to the set of equations (1); $\overrightarrow{k}$ is the wave vector and $D(\overrightarrow{k})$ and I are respectively the dynamical and the identity matrix. We use a standard procedure of diagonalizing it and obtain ω_s the eigenvalues and $\overrightarrow{u_{ns}}$ the eigenvectors. The curves $\omega_s = \omega_s(\overrightarrow{k})$ are the phonon dispersion curves of the crystal.

Graphite

The lattice of a crystal, with N atoms in the basis of atoms, is considered as sum of N sublattices. A sublattice contains only one atom and has the symmetry of the crystal primitive cell.

We take into account the interactions between atoms in the sublattice and with neighbouring sublattices. All the atoms of a sublattice are supposed to vibrate with the same intensity.

For pristine graphite, the primitive cell contains four atoms labelled A,B,C and D. For graphite we consider only five force constants :

- α_1, α'_1 for first neighbours in-plane interactions;
- α_2 for second neighbours in-plane interactions;
- α_3, α'_3 for first neighbours out of plane interactions.

The four carbon atoms, with three degrees of freedom per atom, transform the set of equations (1) into twelve differential equations which can be represented by a 12 × 12 dynamical matrix :

$$D(\overline{k}) = \begin{pmatrix} A & C^* & E & 0 \\ C & B & 0 & 0 \\ E & 0 & A & C \\ 0 & 0 & C^* & B \end{pmatrix} \tag{4}$$

the matrix elements in (4) are 3 × 3 matrices.

Intercalation compounds

For intercalation compounds we add two force constants related to the first neighbours carbon-intercalate interactions :

- β_1 and β'_1.

For the different compounds we obtain complex dynamical matrices with a dimension between 9 × 9 (for LiC_2) and 81 × 81 (for the MC_8 three sites structure).

RESULTS

To approximate correctly the phonon dispersion curves of the different compounds we use the force constants shown in table 2.

Table 2 : Atomic force constants (in $N.m^{-1}$)

Compound	Carbon-carbon interactions					Carbon-intercalate interactions	
	α_1	α'_1	α_2	α_3	α'_3	β_1	β'_1
Graphite	505.1	84.4	73.7	5.92	0.72	...	...
LiC_6, LiC_2	568.7	21.5	68.2	2.13	0.245	27.95	3.47
CaC_6, BaC_6	486.0	81.4	66.4	3.51	0.295	3.2	0.15
SrC_6, SmC_6	"	"	"	"	"	"	"
EuC_6, YbC_6	"	"	"	"	"	"	"
CsC_8	491.5	83.6	66.7	3.51	0.242	5.6	0.35
KC_8	491.5	83.6	66.7	3.51	0.242	3.5	0.25
RbC_8	491.5	83.6	66.7	3.51	0.242	4.2	0.28

With the help of the experimental values for vibration frequencies at the center Γ (graphite and GIC) and zone boundaries A and M (graphite) of the Brillouin zone, we evaluate the atomic force constants introduced in the dynamical matrices. For graphite we choose two frequencies in Γ, one in A and two in M; the atomic force constants obtained are shown in table 2.

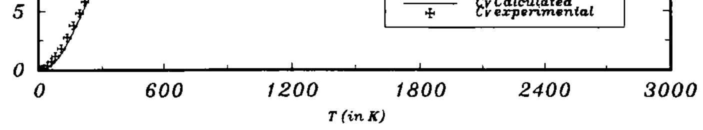
We diagonalize the dynamical matrix and then we evaluate the atomic force constants as a function of the choosen frequencies. For the MC_8 G.I.C. we suppose that the atomic force constants for the carbon-carbon interactions are very close to those in pure graphite. With the help of the phonon dispersion curves of these compounds measured with inelastic neutron diffusion by Zabel [7]-[12], we evaluate the carbon intercalate atomic force constants. And then using the Raman measurement performed by Solin [13] we calculate the exact atomic force constants for the carbon-carbon interactions.

With the help of density of states $g(\nu)$ and following formula :

$$C_v = k_B \sum_{\nu_i} \left(\frac{h\nu_i}{k_B T}\right)^2 \frac{e^{h\nu_i/k_B T}\, g(\nu_i)}{\left(e^{h\nu_i/k_B T} - 1\right)^2} \tag{5}$$

we evaluate the specific heat for the compounds. The specific heat of graphite obtained by the previous relation (5) is in good agreement with the experimental measurements performed by De Sorbo and Tyler[14], Spencer[15],Krumhansl and Brooks[16] and theoretical calculations by Young and Koppel[17] see figure 1.

Figure 1 : Specific heat of graphite



Graphite is characterized by an anomalous specific heat for low temperatures : we observe a T^2 behaviour, like in theoretical calculations for two dimensional crystals, instead of the ordinary T^3 law for three dimensional compounds. This behaviour is related to the high anisotropy of the lattice. To show this T^2 dependence we approximate the specific heat C_v(for temperatures below 160 K) with a power law :

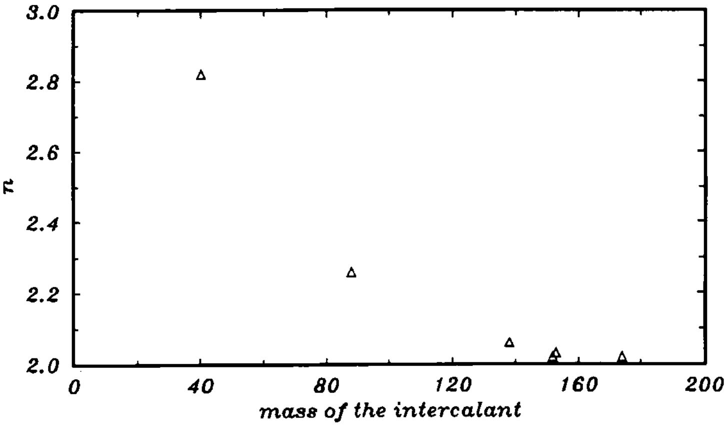
$$C_v = \beta T^n \tag{6}$$

The best fitting (for a lowest χ^2 criterion) gives the variational parameters in table 3. We observe (for MC_6 two sites or MC_8 three sites) that the bigger the mass, the higher the anisotropy (linked to the exponent n). When the mass of the intercalate atoms becomes very large (up to 173 for Yb) the intercalate plane can not transmit the vibrations of a carbon plane to the next plane and then the system is a succession of planes vibrating independently one to the other and the structure becomes very anisotropic and 2-dimensional.

Table 3 : 2D character of the compounds.

Graphite	LiC_6	LiC_2	CaC_6	SrC_6	BaC_6	SmC_6	EuC_6	YbC_6	KC_8	RbC_8	CsC_8
2.01	2.83	2.97	2.82	2.26	2.06	2.03	2.02	2.03	2.98	2.52	2.49

Figure 2 : evolution of the 2D character for MC_6 compounds



CONCLUSIONS

Even if the model is simple (only five atomic force constants for graphite and seven for its intercalation compounds) the results obtained from a thermodynamical point of view (specific heat and Debye temperature) are in good agreement with available experimental values.

We also show the anisotropic behaviour of specific heat of graphite and intercalation compounds with heavy intercalate. We presume that the mass of the atom do not permit at an intercalate plane to transmit the motion of a graphitic plane to the next and so all the planes vibrate independently and then those types of crystal (BaC_6, SmC_6, EuC_6 and YbC_6) possess a quasi-bidimensionnal behaviour.

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