

## Frequency distribution function and critical points for phonons in graphite

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**Abstract.** A molecular force field for the study of the dynamics of graphite has been reported earlier (Mani and Ramani 1974). In the present paper we present calculations of the single phonon density of states and the lattice specific heat. Most of the peaks in the frequency distribution function have been identified and classified using symmetry-required critical points. The validity of the force field used has also been discussed.

**Keywords.** Phonons in graphite; critical points; frequency distribution function; specific heat.

### 1. Introduction

In a previous paper (Mani and Ramani 1974), we have shown that the description of the force field in graphite in terms of molecular force-constants transferred from naphthalene leads to a better understanding of the phonon-dispersion curves in graphite. The valence-force field suggested previously seems to give a better physical picture of the dynamics of a homopolar crystal like graphite than the axially-symmetric (AS) model of Nicklow *et al* (1972), which does not distinguish between the in-plane bending and out-of-plane bending vibrational modes. The valence-force constants (VFC) reported previously are used here to construct the single-phonon density of states in graphite. The frequency-distribution function has been calculated following the linear-extrapolation method of Gilat and Raubheimer (1966). Most of the peaks in the frequency-distribution function have been identified and classified by symmetry-required critical points. Using the calculated frequency-distribution function, the specific heat of graphite is calculated as a function of temperature.

### 2. The force field

We summarise the results of our earlier work below. In this, the dynamical matrix for graphite was set up in terms of tensor-force constants, interactions up to third neighbours in plane and first neighbours out of plane being considered. Of the twelve force constants, those pertaining to the first two neighbours in plane were expressed in terms of the bond-stretching, in-plane and out-of-plane bending constants of naphthalene. The third neighbour constants were determined by

a fit to the observed  $\Gamma_3^+$  mode. The first neighbour out-of-plane constants were obtained from the sound velocities along the  $c$ -axis.

The major differences between these calculations and those of Nicklow *et al* (1972) occur for the  $\Gamma_2^-$  and  $\Gamma_3^+$  modes, and their subsequent variation through the Brillouin zone. We attributed this difference to the axially symmetric (AS) model of Nicklow *et al* (1972). Axial symmetry around a bond in the plane demands that the force constants for in-plane and out-of-plane displacements be equal. In our calculations, the ratio of the in-plane to the out-of-plane constant is 0.10 or less, depending on the neighbour considered. The result is that the  $\Gamma_2^-$  and  $\Gamma_3^+$  modes have frequencies of 642  $\text{cm}^{-1}$  and 629  $\text{cm}^{-1}$ , respectively, as compared to  $1395 \pm 10 \text{ cm}^{-1}$  obtained by Nicklow *et al* (1972). Considering the anisotropic nature of graphite and our good fit to the observed data, we were led to conclude that AS conditions would not apply to graphite.

Our attention has since been drawn to the work on graphite by Ahmadiéh and Rafizadeh (1973) which we had overlooked in our earlier work. These authors have attempted to obtain the dispersion curves and elastic constants of graphite, using Lennard-Jones two-body potentials. The calculation is characterised by two sets of Lennard-Jones parameters, one for the interactions between atoms in different planes and the other for interactions between atoms in the same plane. The calculated dispersion curves differ from experiment in two vital respects. The major elastic constants are very poorly fitted, with errors of over 50%. The other discrepancy is the failure to obtain the parabolic variation with wave-vector of transverse acoustic phonons in the basal plane (Nicklow *et al* 1972, Mani and Ramani 1974). Although recourse has been taken in the work of Ahmadiéh and Rafizadeh to the vibrational frequencies of benzene, the defects mentioned above overshadow the concept of force constant transference. We are thus inclined to believe that any restriction on the force field will lead to erroneous results for graphite.

### 3. Single-phonon density of states

The single phonon density of states  $g(\omega)$  of graphite with the above force field has been obtained using the linear-extrapolation method of Gilat and Raubenheimer (1966), Raubenheimer and Gilat (1967). We have slightly modified this method by filling the irreducible part of the Brillouin zone with identical rectangular prisms alone, in contrast to Raubenheimer and Gilat (1967), who used triangular prisms for the boundaries of the zone. Accidental degeneracies and critical points not required by symmetry were avoided by repeating the calculation for different mesh sizes. The unsmoothed plot of  $g(\omega)$  thus obtained is given in figure 1. The computations were performed on a CDC 3600 computer, the small noise in the function  $g(\omega)$  being due to the small number of mesh points used ( $\sim 1000$ ). Limitations of computational time prohibited the use of a larger number of mesh points.

### 4. Correlations with the symmetry-required critical points

The critical points for the phonon spectrum have been obtained by standard methods (Phillips 1956). They are listed in table 1, along with the corresponding values of the frequencies. The notation for the irreducible representations of the space group of graphite,  $D_{6h}^4$ , is that of Slater (1965).

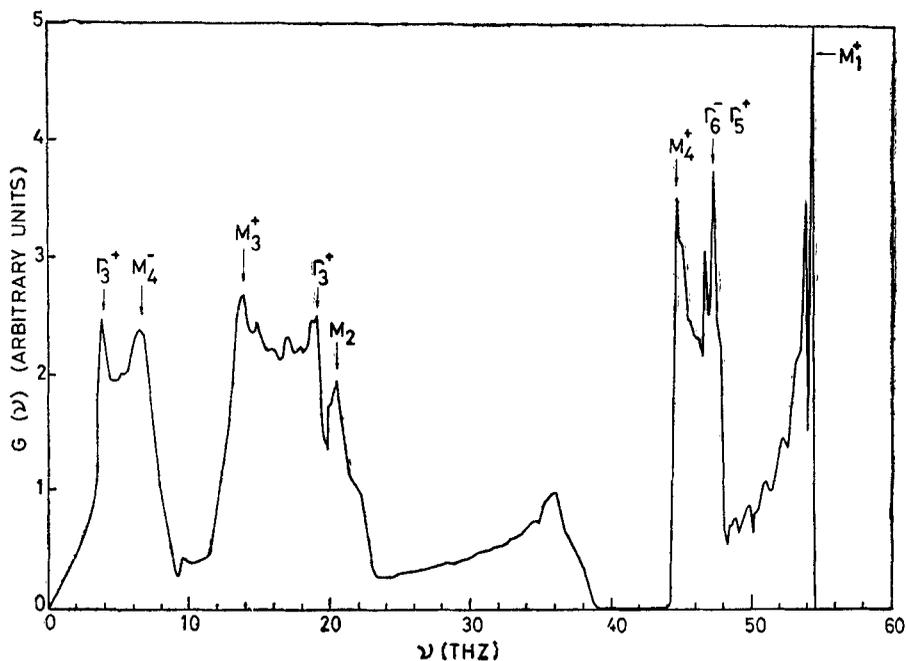


Figure 1. Frequency distribution function (using GR method).

Table 1. Analytical critical points in graphite (by symmetry)

Critical point	Phonon species	Frequency (THz)	Phonon species	Frequency (THz)
$\Gamma$	$\Gamma_4^-$	18.9	$\Gamma_6^-$	47.2
	$\Gamma_3^+$	3.7	$\Gamma_5^+$	47.3
	$\Gamma_3^+$	19.3	$\Gamma_5^+$	1.3
A	$A_1$	2.7	$A_3$	0.9
	$A_1$	19.1	$A_3$	47.3
M	$M_3^-$	20.6	$M_3^+$	13.4
	$M_3^-$	36.6	$M_3^+$	7.5
	$M_4^-$	6.6	$M_4^+$	44.1
	$M_3^-$	20.0	$M_4^-$	12.8
	$M_1^+$	54.6	$M_3^-$	36.6
K	$K_4$	9.6	$K_2$	9.2
	$K_1$	39.2	$K_3$	39.2

Table 2. Correspondence between peaks in frequency distribution function and symmetry-required critical points

Observed peak values (THz)	Identified critical points (see table 1)	Observed peak values (THz)	Identified critical point (see table 1)
3.8	$\Gamma_3^+$	44.4	$M_4^+$
6.6	$M_4^-$	46.4	..
13.8	$M_5^-$	47.0	$\Gamma_6^-, \Gamma_5^+$
19.0	$\Gamma_3^+, \Gamma_2^-$	53.4	..
20.4	$M_3$	53.8	$M_1^+$
35.8	$M_4^-, M_3^-$		

The correspondence between the peaks in the calculated density of states and the singularities expected due to critical points is given in table 2. The agreement is seen to be good. Some of the critical points do not contribute to singularities in the density of states, which is due to the fact that at such points different types of singularities annul each other (Van Hove 1963). Singularities also exist which are not assignable from symmetry-required critical points alone; in this paper we do not attempt to exhaust all such critical points.

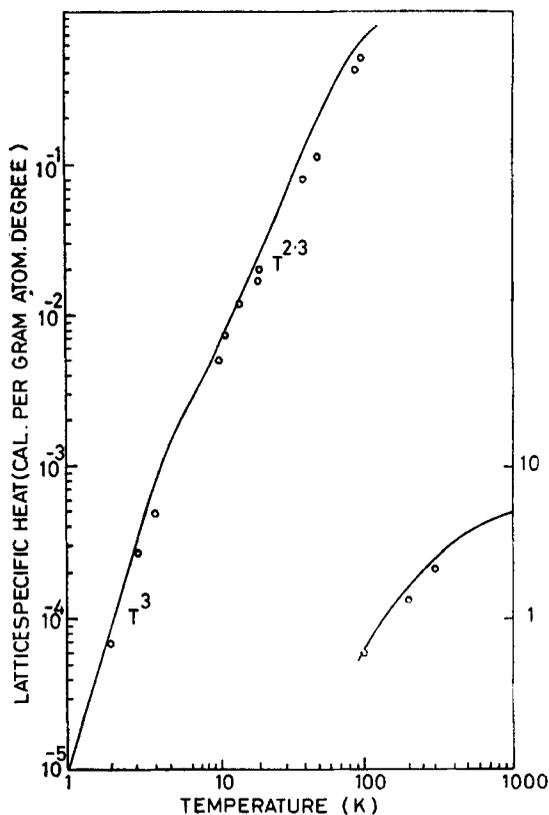


Figure 2. Lattice specific heat as a function of temperature on a log-log scale. The experimental points are from DeSorbo (1953); DeSorbo and Nichols (1958).

A comparison of the calculated frequency distribution with the inelastic neutron scattering data of Egelstaff and Cocking (1960) and Haywood and Thorson (1962) is not fruitful, since the neutron data give only a general envelope to the distribution function. The presence of a peak at 3.8 THz is in agreement with our value for the  $\Gamma_3^+$  critical point. The frequency distribution derived here shows much greater weightage and structure in the low frequency region when compared to the calculations of Nicklow *et al* (1972).

## 5. Specific heat

The lattice specific heat  $C_v$  has been calculated as a function of temperature using the distribution function of figure 1, and is plotted as a function of temperature on a log-log scale (figure 2). The  $T^3$  behaviour at very low temperatures as well as the approximately  $T^2$ -dependence at intermediate temperatures, expected for lamellar solids, are both obtained. However, our calculated values are slightly larger than the ones obtained experimentally throughout, which we attribute to the large weightage accorded to the low frequency modes in the frequency distribution function. Since the question of the  $\Gamma_2^-$  and  $\Gamma_3^+$  modes has not yet been settled experimentally, we have no firm comments to offer regarding this.

## 6. Conclusions

Using the molecular force field previously established for graphite, the phonon-frequency distribution is calculated using the GR-method with a simple network of meshes. Most of the peaks in the frequency-distribution function have been identified and classified as due to symmetry-required critical points. The specific heat of graphite has been calculated as a function of temperature.

## Acknowledgements

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