The effect of two dimensions on the atomic vibrations at the (0001) graphite surface

1991 J. Phys.: Condens. Matter 3 909

(http://iopscience.iop.org/0953-8984/3/8/003)

J. Phys.: Condens. Matter 3 (1991) 909–913. Printed in the UK

The effect of two dimensions on the atomic vibrations at the (0001) graphite surface

S P Tewari and Poonam Silotia
Department of Physics and Astrophysics, University of Delhi, Delhi-110 007, India

Received 14 June 1990, in final form 30 October 1990

Abstract. The recent dynamical model suggested by the present authors is modified to explain the observed experimental results on atomic vibrations of carbon atoms perpendicular to (0001) graphite surface ($\langle u_z^2 \rangle_T$) in the temperature range 0–300 K. The model also yields the detailed calculated values of $\langle u_z^2 \rangle_T$ given by Firey *et al*. It is found that in both cases the atomic vibrations are predominantly two dimensional in character.

1. Introduction

Graphite is a highly anisotropic crystal and can be visualized as made up of a stack of planes weakly coupled to one another. The vibration of a carbon atom in graphite is therefore highly anisotropic. That is, the mean square displacement (MSD) $\langle u_{x,y}^2 \rangle$ of an atom in the basal plane is quite different and much lower than the corresponding MSD $\langle u_z^2 \rangle$ perpendicular to the basal plane at any given temperature. It is expected that $\langle u_z^2 \rangle$ for the plane at the top of the crystal will be quite different from that in the plane located in the bulk. This is indeed so when one compares the experimental results on $\langle u_z^2 \rangle$ obtained by Boato *et al* (1982) for the top layer with those obtained by Hsieh and Colella (1987) in the plane located in the bulk of a graphite crystal. The experimental values of Boato *et al* are much lower than those given by Hsieh and Colella when $T < 100$ K and are somewhat larger for $T > 250$ K. However, Boato *et al* in their paper assert that their reported values suffer from systematic errors and, if these are taken into account, the temperature dependence of the measured values of $\langle u_z^2 \rangle$ would correspond to the temperature dependence of their calculations based on a model which, strictly speaking, corresponds to the plane in the bulk. It is somewhat difficult to accept their proposition particularly because the top layer in the graphite crystal has no layer above it.

The above conclusion is corroborated also by the extensive calculations of Firey *et al* (1983). The calculated temperature-dependent values of $\langle u_z^2 \rangle$ for the top layer turn out to be very different from and higher than the corresponding measurements of Boato *et al* at any given temperature. Even the temperature dependence is not similar to that given by Boato *et al*.

Recently, we have suggested an anisotropic phonon frequency distribution function (FDF) for a planar crystal (Tewari and Silotia 1989), which is valid for the vibrations of a carbon atom when the graphite plane is in the bulk. The calculated values of $\langle u_z^2 \rangle$ turn out to be in reasonable agreement with the corresponding experimental values of Hsieh

0953-8984/91/080909 + 05 $03.50

and Colella in the temperature range 0–300 K. It is therefore worthwhile to investigate the change in the phonon FDF when the graphite layer happens to be at the top of the crystal, particularly with respect to two-dimensional, i.e. planar, modes.

2. Mathematical formalism

The expression for the MSD (Tewari and Silotia 1989) of an atom in the ith direction in terms of the phonon FDF in a harmonic approximation is as follows:

$$\langle u_i^2 \rangle = \frac{\hbar}{MN} \int_0^{\nu_{mi}} \nu^{-1} g_i(\nu) \left(\frac{1}{2} + \frac{1}{\exp(h\nu/k_B T) - 1} \right) d\nu \tag{1}$$

where $i = z$ gives $\langle u_z^2 \rangle$ and $i = x, y$ yields $\langle u_{x,y}^2 \rangle$ and where the other symbols have their usual meanings.

The suggested phonon FDF $g_z(\nu)$ along the c axis is as follows:

$$g_z(\nu) = \begin{cases} A_z \nu^{n(=2)} & 0 \leqslant \nu \leqslant \nu_{0z} \\ B_z \nu & \nu_{0z} \leqslant \nu \leqslant \nu_{mz} \\ 0 & \nu > \nu_{mz}. \end{cases} \tag{2}$$

The values of A_z and B_z can be determined using firstly the continuity of $g_z(\nu)$ at $\nu = \nu_{0z}$ and secondly the total number of modes equal to N.

Substituting equation (2) into equation (1), one obtains the following expression for $\langle u_z^2 \rangle$:

$$\langle u_z^2 \rangle = \frac{\hbar^2}{Mk_B} \frac{\Delta_z}{\theta_{0z}} \left[\left(\frac{1}{\delta_z} + \frac{1-n}{n} \right) + \frac{2}{\varepsilon_3^n} \int_0^{\varepsilon_3} \frac{x^{n-1}}{\exp x - 1} dx + \frac{2}{\varepsilon_3} \int_{\varepsilon_3}^{\varepsilon_2} \frac{1}{\exp x - 1} dx \right] \tag{3}$$

where

$$\delta_z = \theta_{0z}/\theta_{mz} \qquad \Delta_z = [1/\delta_z^2 - (n-1)/(n+1)]^{-1}$$

$$\varepsilon_3 = \theta_{0z}/T \qquad \varepsilon_2 = \theta_{mz}/T.$$

For $n = 2$, equation (3) reduces to the expression for $\langle u_z^2 \rangle$ when the graphite plane is in the bulk (Tewari and Silotia 1989). There is hardly any change in the dynamical modes of the basal plane when the graphite surface is at the top or in the bulk (Oshima *et al* 1988).

3. Results and discussion

It has been found that $h\nu_{0z}/k_B = \theta_{0z} = 60$ K and $h\nu_{mz}/k_B = \theta_{mz} = 840$ K (Tewari and Silotia 1989); when these were utilized to evaluate $\langle u_z^2 \rangle$ in bulk, they yielded values which were in reasonable agreement in the entire temperature range from 0 to 300 K with the

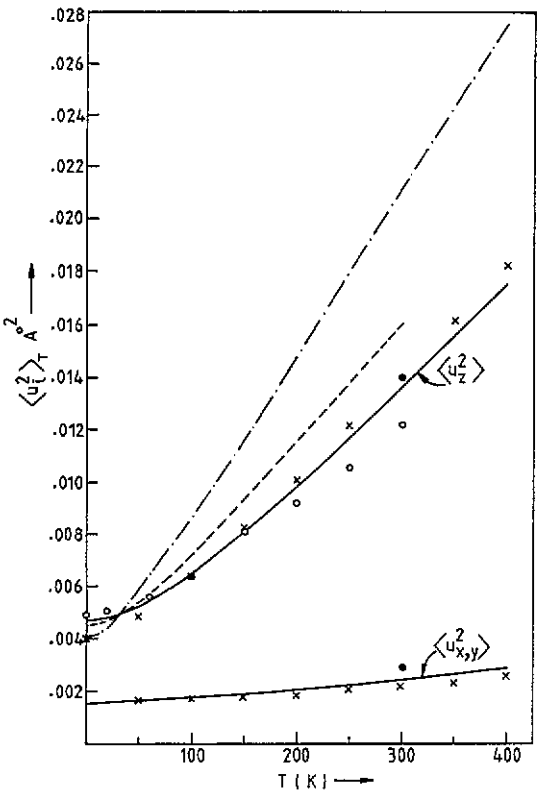

Figure 1. Comparison of the calculated values of the temperature-dependent MSD with the experimental results of a carbon atom along the c axis ($i = z$) and in the basal plane ($i = x, y$) when the graphite plane is located in the bulk: ○, experimental data (Hsieh and Colella 1987); ●, experimental results (Chen and Trucano 1978); ×, values calculated by Firey *et al* 1983) (not experimental results); – – –, values calculated by Boato *et al* (1982); ———, present calculations based on the suggested dynamical model; — · —, values calculated by Firey *et al* when the graphite plane is at the top of the graphite crystal.

corresponding measured values of Hsieh and Colella as is also evident from figure 1. We have also plotted in the figure as crosses the values calculated by Firey *et al* (1983), which are in good agreement with our calculated values in the entire temperature range from 0 to 400 K except at around $T = 0$ K. The value of $\langle u_z^2 \rangle$ at 300 K obtained by Chen and Trucano (1978) using x-ray diffraction measurements is also in agreement with our results, as is shown in the figure. (For the sake of completion, we have also shown our calculated values of $\langle u_{x,y}^2 \rangle$ (Tewari and Silotia 1989) together with the measured value of Chen and Trucano at 300 K and the calculated values of Firey *et al* at various temperatures. As is clear from the figure, these are in good agreement with one another.) The calculated values of $\langle u_z^2 \rangle$ given by Boato *et al* and shown by the broken curve are quite different from the experimental values of Hsieh and Colella, our calculated values and those given by Firey *et al* for all temperatures greater than 80 K. Figure 1 also shows the values of $\langle u_z^2 \rangle$ calculated by Firey *et al* when the graphite surface happens to be at the top of the crystal. It is clear that these $\langle u_z^2 \rangle$ are quite different in most of the temperature range. It may be noted that the assertion of Boato *et al* that there is a negligible change

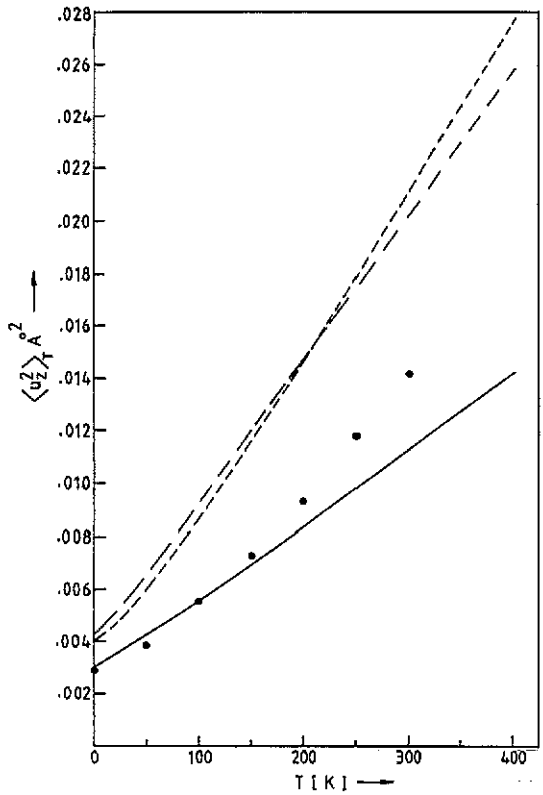

Figure 2. Comparison of the calculated values with the experimental results of the MSD in the c direction of a carbon atom when the graphite (0001) surface is located at the top of the graphite crystal: ●, experimental results of Boato *et al* (1982); – – –, values calculated by Firey *et al* (1983); ———, present dynamical model calculations for $\theta_{mz} = 1300$ K and without any change in θ_{0z} (60 K) and n (= 1.1); — —, present dynamical model calculations for $\theta_{mz} = 930$ K without any change in θ_{0z} (= 60 K) and n (= 1.1). (For the meaning of the symbols, see the text.)

in $g_z(\omega)$ when the graphite layer is in the bulk or at the top of the crystal is not tenable. For, if it were so, $\langle u_z^2 \rangle$ in the two cases should be the same at any temperature.

Assuming that the measured values reported by Boato *et al* are reliable (they mention in their paper that these values are accompanied by large systematic errors), we have tried to reproduce these by varying n in equation (2). The clue to the variation in n is provided by the fact that the measurements of Boato *et al* are predominantly related to surface dynamics where the bulk plays little role. (For an isolated surface the value of n will be i). The experimental study of the dispersion relation of surface phonons of graphite by Benedek *et al* (1986) also indicates such a change in n. We therefore decreased the power $n = 2$ of ν in the first part of the spectrum, i.e. in the frequency range $0 \leqslant \nu \leqslant \nu_{0z}$. When the value of n decreases, the FDF gets spread to a higher value of ν_{mz} since the total number of modes, equal to N does not change whether the surface is at the top or in the bulk. It is found that, when the power of ν is reduced to 1.1 and the value of θ_{mz} is increased to 1300 K without changing the value of θ_{0z}, this yielded the values of $\langle u_z^2 \rangle$ shown by the full curve in figure 2 together with the corresponding

experimental results indicated by full circles of Boato *et al* in the temperature range 0–300 K. The calculated values are in good agreement with the corresponding experimental results in the temperature range 0–200 K. For temperatures higher than 200 K, the calculated values are lower than the corresponding experimental results (Boato *et al* 1982) but the maximum difference is about 19% at $T = 300$ K. We therefore find that the experimental results of Boato *et al* for surface atoms located at the top of the graphite crystal can be reasonably well explained by the suggested phonon FDF with $\theta_{0z} = 60$ K, $\theta_{mz} = 1300$ K and $n = 1.1$. Thus, it is clear that, in the dynamics of surface atoms, almost all the modes are two dimensional in character. Only very-low-energy modes up to $\theta_{0z} = 60$ K have dimensions slightly greater than two, which also implies a very weak coupling of surface atoms to those lying in the lower surfaces. This is in quite a contrast to the dynamics of the graphite atoms perpendicular to the basal plane in bulk where three-dimensional modes are present up to 60 K. Further, the density of low-energy modes of these surface vibrations is also substantially smaller than that in the bulk.

However, the values of Firey *et al* are quite different from those of Boato *et al* and, in order to reproduce their values based on our model, we find that n has to be 1.1 but θ_{mz} is now 930 K as against 1300 K obtained earlier. The comparison between the calculated values and the results of Firey *et al* are also shown by the broken curves (long dashes and short dashes, respectively) in figure 2. The agreement between the two is reasonable. These results also indicate the predominantly two-dimensional character of the surface phonons.

If one plots the ratio $R = \langle u_z^2 \rangle_{surface} / \langle u_z^2 \rangle_{bulk}$, one finds that R given by Firey *et al* is greater than unity even at $T = 0$ K and becomes approximately 1.5 at around 300 K. If the suggestions of Boato *et al* are correct, the ratio R should have been unity throughout the temperature range.

4. Conclusion

We conclude that the observed atomic vibrations of the graphite atoms perpendicular to the surface as measured by Boato *et al* or given by Firey *et al* in the temperature range 0–300 K can be reasonably well explained by using the suggested phonon FDF which takes account of the predominant presence of surface modes.

Acknowledgment

PS is grateful to CSIR, New Delhi for financial assistance.

References

Benedek G, Brusdeylins G, Heimlich C, Toennies J P and Valbusa U 1986 *Surf. Sci.* **178** 545–52
Boato G, Cantini P, Salvo C, Tatarek R and Terreni S 1982 *Surf. Sci.* **114** 485–97
Chen R and Trucano P 1978 *Acta Crystallogr.* A **34** 979–82
Firey B, de Wette F W, de Rouffignac E and Alldredge G P 1983 *Phys. Rev.* B **28** 7210–8
Hsieh S M and Colella R 1987 *Solid State Commun.* **63** 47–50
Oshima C, Aizawa T, Souda R, Ishizawa Y and Sumiyoshi Y 1988 *Solid State Commun.* **65** 1601–4
Tewari S P and Silotia P 1989 *J. Phys.: Condens. Matter* **1** 7535–41