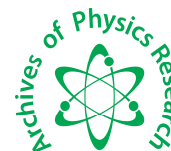




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### Diffusion of intercalant atoms in stage-2 $\text{CsC}_{24}$ and $\text{RbC}_{24}$ graphite intercalation compounds

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#### ABSTRACT

Quasi-elastic neutron scattering experiments on alkali-metal graphite intercalation compounds are analyzed by treating the alkali-metal system as a viscous and dense two-dimensional liquid. The coherent scattering function and its full width at half maximum is analyzed by treating the potential between the intercalant atoms as a sum of two potentials. We have studied intercalant atoms diffusion in stage-2  $\text{CsC}_{24}$  and  $\text{RbC}_{24}$  graphite intercalation compounds. We have shown that in the dynamic structure factor there is a competition between a single particle potential, due to the graphite bounding layers, which favours a registered for the alkali metal intercalant, and a pair potential between alkali atoms which prefers an unregistered phase. The explicit temperature dependence in the dynamic structure factor enters through the kinetic terms in the frequency moments. The other inputs like pair correlation function  $g(r)$  and the Fourier coefficients in the modulated potential have been taken from the experimental measurements at  $300^0\text{k}$ . We have taken them to be same at all values of the temperatures. This introduces appreciable error, especially at large temperatures. That is the reason why our calculated  $\Delta\omega$  show considerable error when compared with experimental measurements at high temperatures.

**Keywords:** Graphite intercalation compounds, quasi-elastic coherent scattering width, frequency moments, Dynamic structure factor, pair correlation function.

#### INTRODUCTION

Graphite intercalation compounds (GIC) exhibit the unusual phenomenon of staging where nearest pairs of guest layers are interspersed by graphite layers in a stacking sequence that repeats to yield long-range order in the c-axis direction. Interest in the study of GIC's is growing because the graphite layers provide galleries into which a wide variety of guest species can enter to form the donor as well as acceptor GIC's [1-4]. Much of the interest was initially motivated by reports of highly anisotropic electronic transport [5], and the complex structural configuration [6-7] of intercalant molecules within the graphic host.

Attention to diffusional response has been drawn by the quasi-elastic neutron scattering experiments of Zabel et al [8] on  $\text{RbC}_{24}$  and  $\text{CsC}_{24}$ . The experiments performed at various temperatures in the disordered phase region indicate that the quasi-elastic peak is narrow and can be followed experimentally up to wave vectors lying well beyond the main peak of the in-plane structure factors. The temperature and wave-vector dependence of the widths of the spectra (full width at half maximum) show that the line broadening is due to alkali-metal in-plane mobility. Both similarities and differences emerge when these observations are compared with those on three-dimensional (3D) liquid Rb [9]. Therefore, from a dynamical point of view, suggestions have been made by Zabel and co-workers [8] whether the disordered alkali-metal layers may be characterized as highly viscous and dense 2D fluids, the "floating solid" model proposed by Nelson and Halperin [10], or the hopping motion in a lattice gas. So far to the best of our knowledge not much theoretical work has been done in this direction.

A preliminary lattice gas calculation with nearest-site hopping over a lattice without interaction except the avoidance of double-site occupancy was carried out by Chaturvedi and Toshi[11] to study the frequency-dependent diffusional response. The liquid like structural disorder in the quasi-elastic coherent scattering width was incorporated by assuming a spread in jump lengths around a preferred set of jumps. Physically this means that particles oscillate around its mean position before they hop to a nearest- neighbor site.

The intercalated alkali-metal atoms are assumed to interact via a screened Coulomb potential, obtained earlier by Plischke [12]. The structural and dynamical properties of intercalants in graphite intercalation compounds are governed by a competition between the intercalant-graphite interaction and the intercalant-intercalant interactions. The frustration exhibited in the partially ordered low temperature structure of stage-2 heavy-alkali-metal GIC's, for example, full width at half maximum is a consequence of this competition.

A knowledge of these potentials is therefore essential for a theory of diffusion in the high temperature quasi-2-dimensional intercalant liquid of the freezing (melting) transition at low temperature or of the temperature-dependent phonon spectra. The selection of potentials for computer simulation [13-15] has been guided by

- (i) Two-dimensional electron-gas-model calculations of the intercalant pair potential [12] and
- (ii) The modulated intercalant-host potentials extracted from X-ray measurements by Smith et al [16] have also derived this potential for Rb and K GIC's from total energy calculations within the local-density-functional-theory (LDFT) frame work. The predicted potential for stage-2 Rb GIC is in excellent agreement with potentials derived from X-ray experiments, although some discrepancy was found for stage-2 K GIC.
- (iii) Our objective in the present paper is to study diffusion in the quasi-two-dimensional intercalant liquid of stage-2 RbC<sub>24</sub> and CsC<sub>24</sub>. We analyze the coherent scattering function and its full width at half maximum by treating the potential between the intercalant atoms as a sum of two potentials.

The outline of the paper is as follows. In Sec. II we describe our model and use Mori-Zwanzig projection operator technique to obtain the dynamic structure factor. As a time evolution operator the usual Liouville operator is replaced by the Kolmogorov operator. In Section III, we describe the potential as a sum of two potentials. In section IV we calculate the frequency moments with this potential. In section V we calculate the Dynamic structure factor. Numerical results and the conclusions are summarized in section VI.

### The Model

The coherent dynamics structure factor  $S(k, \omega)$ , is the Fourier Transform of the density-density correlation function.

$$S(k, \omega) = (2\pi N)^{-1} \int e^{i\omega t} \langle \rho(k, t) \rho(-k, 0) \rangle dt \quad (1)$$

$$\text{With } \rho(k, t) = \sum_{i=1}^N e^{ik \cdot r_i(t)} \quad (2) \text{The static structure factor } S(k) \text{ is then given by}$$

$S(k) = N^{-1} \langle \rho(k) \rho(-k) \rangle$  (3) Where  $\rho(k)$  denotes the  $t=0$  value of  $\rho(k, t)$  and  $\langle \dots \rangle$  is the ensemble average. The density correlation function can be expressed in terms of the time evaluation operator  $L$  as  $\rho(k, t) = e^{Lt} \rho(k)$  (4)

$$\text{Where } L = \sum_{j=1}^N \left[ v_j \frac{\partial}{\partial r_j} - \frac{1}{m} \frac{\partial V}{\partial r_j} \frac{\partial}{\partial v} \right] \quad (5)$$

Where  $V_j$  is the velocity of the  $j^{\text{th}}$  atom and  $V$  is the interaction Potential.

In order to obtain  $S(k, \omega)$  from Mori-Zwanzig projection operator technique one uses either the memory function approach or the continued fraction method. We use the later approach and express the Laplace Transform of the density correlation function as the infinite continued fraction as

$$\varphi(k, z) = \frac{a_0}{z + b_1 \frac{a_1}{z + b_2 \frac{a_2}{z + \dots + \frac{a_{p-1}}{z + R_p(z)}}}} \quad (6)$$

$$\text{Where } \varphi(k, z) = N^{-1} \int_0^\infty e^{-zt} \langle \rho(k, t) \rho(k) \rangle dt, \quad \text{Re}z > 0 \quad (7)$$

is related to the dynamic structure factor as

$$S(k, \omega) = \frac{1}{\pi} \text{Re} \varphi(k, z = -i\omega) \quad (8)$$

The coefficient  $b_p, a_p$  are defined as

$$b_p = -\langle A_{p-1}^* L A_{p-1} \rangle \cdot \langle A_{p-1}^* A_{p-1} \rangle^{-1} \quad (9)$$

$$a_p = \langle A_p^* A_p \rangle \cdot \langle A_{p-1}^* A_{p-1} \rangle^{-1} \quad p=1,2,3,\dots \quad (10)$$

Here  $A_p$  denotes the  $t=0$  value of the  $p^{\text{th}}$  order random force and  $A_0 = \rho(k)$ . Here  $a_0$  is the static factor  $S(k)$ . The coefficients  $a_p$  and  $b_p$  are related to the frequency moments of the density correlation function  $S(k, \omega)$ .

In applying the continued fraction expansion to the calculation of  $S(k, \omega)$  one faces two problems. First, as one proceeds to higher stages ( $p \geq 3$ ) the coefficients  $a_p$  and  $b_p$  involve higher-order frequency moments which in turn requires the knowledge of the third and higher-order static correlation functions. These correlations are not known a priori. The second is to find a suitable approximation for the remainder part,  $R_p(z)$ , of the infinite continued fraction. In this paper we shall terminate the continued fraction at  $p=3$  by making the assumption that two consecutive terms, that is  $R_p(z)$  and  $R_{p+1}(z)$ , which are connected by

$$R_p(z) = b_p + \frac{a_p}{z + R_{p+1}(z)} \quad (11)$$

are approximately equal. This leads to a quadratic equation for  $R_p(z)$  with solutions

$$R_p(z) = \frac{1}{2} [-Z + b_p \pm \{(Z + b_p)^2 - 4a_p\}^{\frac{1}{2}}] \quad (12)$$

## II. Interionic Potential

The alkali metal atoms in graphite donate their valence electron to the carbon layers and interact via a screened Coulomb potential. The electrostatic potential energy  $V(r)$  of a pair of ions of charge  $e$ , distance  $r$  apart, midway between the two similar carbon layers has been calculated by Plischke [17] as

$$V(r) = \frac{e^2}{k_0} \left[ \frac{1}{r} - S(r) \right] \quad (13)$$

The explicit expression for the screening contribution  $S(r)$  has been obtained by Plischke [12] following the treatment of Visscher and Falicov [18]. The dielectric constant  $K_0$  may be treated as a parameter or can be taken as unity; we have taken  $K_0=1$ . The other contribution to the potential energy is the graphite modulation potential induced in the alkali metal liquid. Recently Fan et al [13-14] and Karnita Kahara *et. al* [19] have tested this potential in the molecular dynamics simulation of liquid Rb in graphite and found an anisotropic  $S(q)$  in complete agreement with experiments [20].

The total potential energy of the intercalant atoms can be expressed as

$$U = \sum_{i \neq j} V(r_{ij}) + \sum_i V_m(r_i) \quad (14)$$

Where  $V(r)$  is the intra-layer screened pair Coulomb potential and  $V_m(r)$  is the modulated single-particle periodic potential due to graphite substrate. The in-plane modulation potential  $V_m(r)$ , may be written as [21]

$$V_m(r) = \sum_{H,K} V_{HK} e^{iG_{HK} \cdot r} \quad (15)$$

Where  $G_{HK}$  is the basal-plane vector of the graphite reciprocal lattice and  $V_{HK}$  is the set of Fourier coefficients. In the HK.0 basal-plane the reciprocal lattice vector  $G_{HK}$  can be written as

$$G_{HK} = Hb_1 + Kb_2 \quad (16)$$

Where H,K are integers and  $b_1, b_2$  are the two-dimensional hexagonal reciprocal lattice vectors. There are three basal-plane reciprocal lattice vectors.

$$b_1 = \frac{2\pi}{\sqrt{3}a} (\sqrt{3}\hat{x} - \hat{y}) \quad (17)$$

$$b_2 = \frac{4\pi}{\sqrt{3}a} \hat{y} \quad (18)$$

$$b_3 = -\frac{2\pi}{\sqrt{3}a} (\sqrt{3}\hat{x} + \hat{y}) \quad (19)$$

The third vector is however not independent because

$$b_3 = -(b_1 + b_2) \quad (20)$$

In the above d is the distance between two carbon atoms in the graphite plane. For different value of the HK.0 the modulated potential can then be expressed as

$$V_m(r) = 2V_{10}[\cos(b_1 \cdot r) + \cos(b_2 \cdot r) + \cos(b_3 \cdot r)] + 2V_{11}[\cos(b_1 - b_2) \cdot r + \cos(b_1 - b_3) \cdot r + \cos(b_2 - b_3) \cdot r] + 2V_{20}[\cos(2b_1 \cdot r) + \cos(2b_2 \cdot r) + \cos(2b_3 \cdot r)] + 2V_{21}[\cos(2b_1 - b_2) \cdot r + \cos(2b_1 - b_3) \cdot r + \cos(2b_2 - b_3) \cdot r] + 2V_{22}[\cos(2(b_1 - b_2)) \cdot r + \cos(2(b_1 - b_3)) \cdot r + \cos(2(b_2 - b_3)) \cdot r] + 2V_{30}[\cos(3b_1 \cdot r) + \cos(3b_2 \cdot r) + \cos(3b_3 \cdot r)] \quad (21)$$

In above equation we have dropped  $V_{00}$  since it gives only constant contribution to the potential energy. Using a nonlinear response theory that accounts for correlations in the liquid, Moss and Coworkers [21-22] determined the modulation potential for 2-D Rb liquid in graphite from a measurement of the Rb contribution to the graphite et Bragg peaks. In Table-1 we have given the evaluated values of  $\beta V_{HK}$  ( $\beta = 1/k_B T$ ) for different values of HK at  $T=300^0\text{k}$ . Within a graphite hexagon the resulting modulated potential is attractive at the center  $V_m(r=0) = -0.0735\text{ev}$  and repulsive at the carbon atoms.

Table-1 Experimental values of the alkali metal (Rb) contribution to the graphite structure factors.

| HK | $\beta V_{HK}$ |
|----|----------------|
| 10 | -0.45          |
| 11 | -0.06          |
| 20 | -0.01          |
| 21 | -0.03          |
| 30 | -0.01          |
| 22 | -0.02          |

While numerically evaluating the potential and its derivatives from the above equation care should be taken because the contribution from Coulombic and screening parts match evenly so that at large distances  $V(r)$  falls off roughly as  $r^{-3}$  with small Friedel oscillations.

### III. Frequency Moments of a Correlation Function

The Frequency Moments say  $S(k, \omega)$ , are defined as

$$\langle \omega^m \rangle = \int_{-\infty}^{\infty} \omega^m S(k, \omega) d\omega, \quad m=0,1,2,\dots \quad (22)$$

Where  $\langle \omega^0 \rangle$  is the static structure factor  $S(k)$

From inverse transform, we can write:

$$\langle \omega^m \rangle = N^{-1} [(-i)^m \frac{d^m}{dt^m} \langle \rho(k, t) \rho(-k, 0) \rangle]_{t=0} \quad (23)$$

T

he frequency moments of  $S(k, \omega)$  are also related to the frequency moments of the normalized longitudinal current correlation function  $\Omega_l^m(k)$  by the relation

$$\Omega_l^m(k) = \langle \omega^{m+2} \rangle / a, \quad a = \left[ \frac{k_B T}{m} \right] k^2 \quad (24)$$

The explicit expression of the second moment of current correlation in terms of the potential energy can be expressed as

$$\Omega_1^2(k) = \frac{3k^2}{\beta m} + N^{-1} \sum_i \langle \frac{\partial^2 U}{\partial x_i^2} \rangle m^{-1} N^{-1} \sum_{i \neq j} \langle \frac{\partial^2 U}{\partial x_i \partial x_j} e^{iq(x_i - x_j)} \rangle \quad (25)$$

After substitution of (14) in (25), we observe that the contribution of the last term in (25) is zero for the modulation potential  $V_m$  as it is a function of either  $x_i$  or  $x_j$ . The contribution of  $V(r)$  is same as calculated by Chaturvedi & Singh [23]. Therefore after some calculations, we get

$$\begin{aligned} \Omega_1^2(k) &= 3a + \frac{\rho}{m} \int dr (\hat{k} \cdot \nabla)^2 V_m(r) + \frac{\rho}{m} \int dr g(r) [1 - \cos(\hat{k} \cdot r)] (\hat{k} \cdot \nabla)^2 V(r) \\ &= [\Omega_1^2(k)]_s + \frac{\rho}{m} \int dr (\hat{k} \cdot \nabla)^2 V_m(r) \end{aligned} \quad (26)$$

Similarly, we have evaluated the fourth frequency moments of the current correlation function. Here we give only the final result which can be expressed as

$$\Omega_1^4(k) = \frac{15 a \rho}{m N} \int dr (\hat{k} \cdot \nabla)^2 V_m(r) + \frac{\rho}{m^2} \int dr [(\hat{k} \cdot \nabla)^2 V_m(r)]^2 + (\Omega_1^4(k))_s \quad (27)$$

Where

$$\begin{aligned} (\Omega_1^4(k))_s &= 15 a^2 + \frac{\rho k_B T}{m^2} \int dr r g(r) \{ 15 (\hat{k} \cdot \nabla)^2 V(r) + 6 k \sin(k \cdot r) (\hat{k} \cdot \nabla)^2 V(r) + \frac{2}{k_B T} [1 - \\ &\cos(k \cdot r)] [(\hat{k} \cdot \nabla V(r))]^2 \} + \\ &\frac{\rho^2}{m^2} \int dr \int dr' g(r, r') \{ 1 - 2 \cos(k \cdot r) + \\ &\cos[k(r - r')] \} (\hat{k} \cdot \nabla) (\hat{k} \cdot \nabla') (\nabla \cdot \nabla') V(r) V(r') \end{aligned} \quad (28)$$

### IV. Dynamic Structure Factor $S(k, \omega)$

To study the dynamics of intercalated atoms in GIC's we use the continued fraction formalism described in section II. The continued fraction is terminated by using the quadratic approximation (equation 12) for the remainder  $R_p(z)$  at  $p=3$ . The coefficients  $a_p, b_p$  are given as

$$b_1 = 0 \quad ; \quad a_1 = \frac{a}{a_0} \quad (29)$$

$$b_2 = 0 \quad ; \quad a_2 = \Omega_1^2(k) - \frac{a}{a_0} \quad (30)$$

$$b_3 = 0 \quad ; \quad a_3 = a_2^{-1} [\Omega_1^4(k) - (a_1 + a_2)^2] \quad (31)$$

Here moments  $\Omega_1^2(k)$  and  $\Omega_1^4(k)$  are given by (26) and (28) respectively. Thus the effect of the modulated potential enters through these moments only.

We have calculated the second and fourth frequency moments of current correlation functions of  $\text{CSC}_{24}$  with aerial density  $\rho = 0.0318(\text{\AA}^0)^{-2}$ , experimentally determined  $g(r)$ , the in-plane modulation potential extracted from X-ray measurements at  $T=300\text{K}$ . In order to see the effect of modulation potential we show in Fig. 1 the value of  $\Omega_1^2(k)/\omega_p^2$  and  $\Omega_1^4(k)/\omega_p^4$  as function of wave number  $k$  at  $280\text{K}$ . The quasielastic coherent scattering width  $\Delta\omega$  are plotted in Figs 2-4 as a function of the wave number  $k$  at different values of the temperature. It is interesting to note that at  $280\text{K}$  the calculated scattering width is quite similar to experimental results. It shows a de-gennes narrowing at the wave number where  $S(k)$  is maximum and flattens at large  $k$ , which is due to the interaction of intercalant atoms with graphite substrate. As the temperature increases the disagreement with the calculated and experimental width also increases. For example, at high temperature ( $618\text{K}$ ) experimental  $\Delta\omega$  shows a second peak at  $k=1.6(\text{\AA}^0)^{-1}$  whereas calculated width becomes flat at large  $k$  for all the temperatures. Also, calculated  $\Delta\omega$  becomes lower as temperature increases. In Fig. 5 we show the dynamic structure factor  $S(k, \omega)$  as a function of  $\omega$  at some selected value of  $k$  at some selected temperature. The shape of  $S(k, \omega)$  is Lorentzian and the quasi-elastic peak becomes narrower as the temperature decreases.

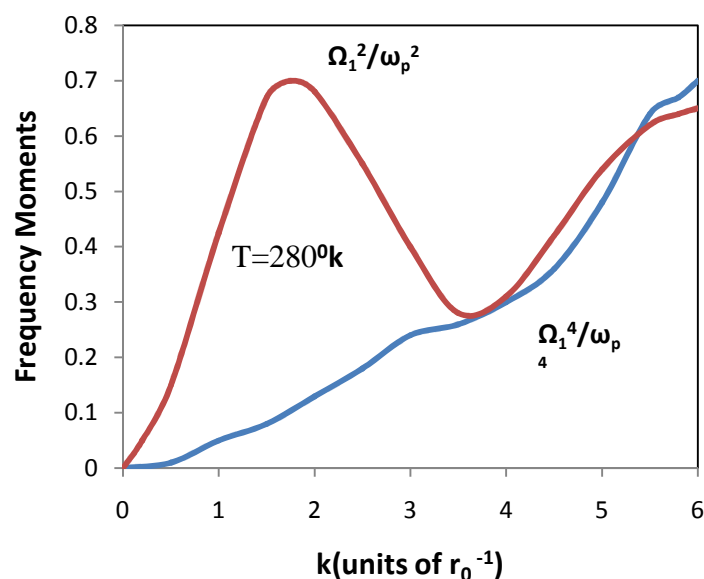


Fig.1 Results of the  $\Omega_1^2(k)$  and  $\Omega_1^4(k)$  as a function of wave number  $k$ .

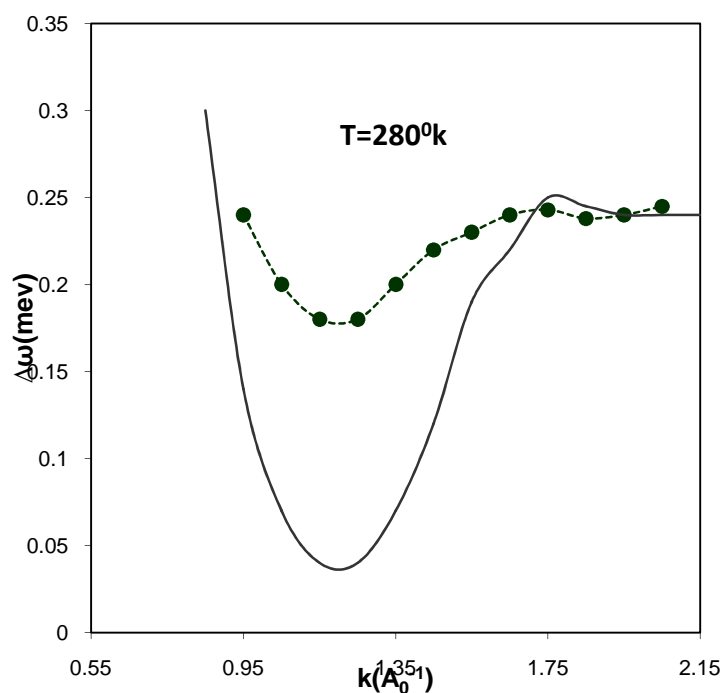


Fig. 2 Coherent scattering width  $\Delta\omega$  as a function of wave number  $k$ . Solid curve shows our result and solid circles denote experimental values. Dashed curves are guide to the eye.

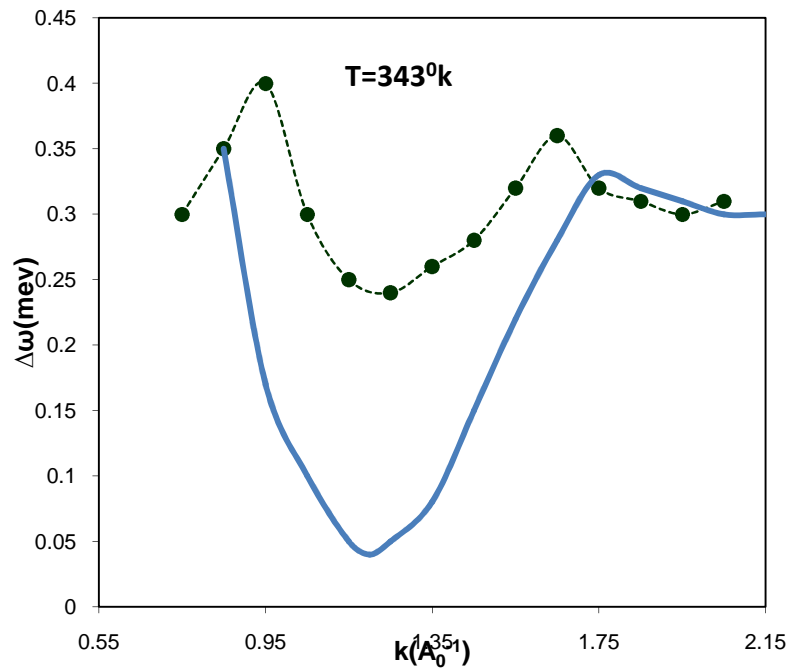


Fig. 3 Coherent scattering width  $\Delta\omega$  as a function of wave number  $k$ . Solid curve shows our result and solid circles denote experimental values. Dashed curves are guide to the eye.

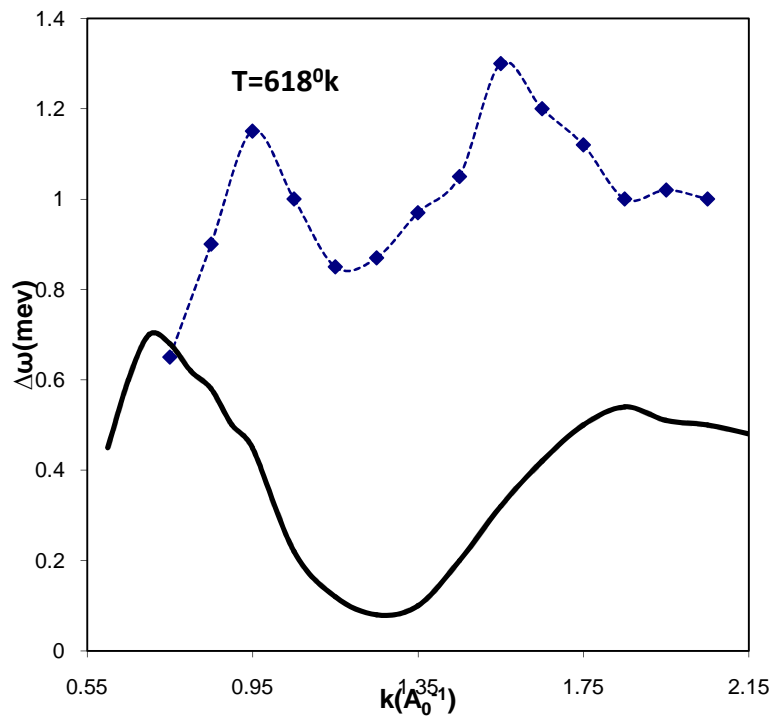


Fig. 4 Coherent scattering width  $\Delta\omega$  as a function of wave number  $k$ . Solid curve shows our result and solid circles denote experimental values. Dashed curves are guide to the eye.

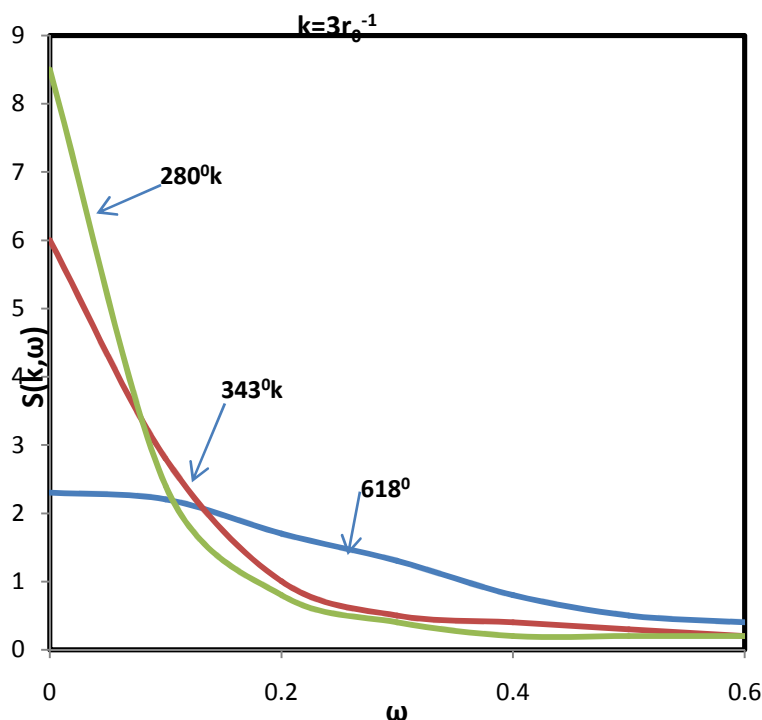


Fig. 5  $S(k, \omega)$  as a function of  $\omega$  for various temperature at one selected  $k$  values. The units of  $k$  and  $\omega$  are  $r_0^{-1}$  and  $\omega_p$  respectively

### CONCLUSION

In this paper we have studied intercalant atoms diffusion in stage-2  $\text{CsC}_{24}$  and  $\text{RbC}_{24}$  graphite intercalation compounds. We have demonstrated that in the dynamic structure factor there is a competition between a single particle potential, due to the graphite bounding layers, which favours a registered for the alkali metal intercalant, and a pair potential between alkali atoms which prefers an unregistered phase. The explicit temperature dependence in the dynamic structure factor enters through the kinetic terms in the frequency moments. The other inputs like pair correlation function  $g(r)$  and the Fourier coefficients in the modulated potential have been taken from the experimental measurements at  $300^\circ\text{K}$ . We have taken them to be same at all values of the temperatures as we do not have the corresponding experimental data. This introduces appreciable error, especially at large temperatures. That is the reason why our calculated  $\Delta\omega$  show considerable error when compared with experimental measurements at high temperatures.

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