

LOW TEMPERATURE HEAT CONDUCTIVITY OF POLYMERS

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ABSTRACT

The phonon conductivity of nylon and polyethylene is calculated in the temperature range 2–4 K on the basis of the extended Callaway model. Plastic deformations appreciably affect the lattice thermal conductivity of polymers in the low temperature range. The static strain fields of dislocation cores and stacking faults scatter the low frequency phonons which give rise to a characteristic depression in the thermal conductivity curve. A good agreement between theoretical and experimental results is obtained in the low temperature range.

PHONON scattering due to the static strainfield dislocations (or complex imperfections which can scatter lattice waves) offers remarkable thermal resistance at a low temperature. The presence of plastic deformations decreases the lattice thermal conductivity of polymers at low temperatures. This phenomenon in polymers is mainly attributed to phonon scattering by stacking faults and to dislocations which emerge during crystal deformation or growth.

The experimental measurements for low temperature phonon heat conductivity of polymers (nylon and polyethylene) reported by Scott *et al*¹ do not offer any theoretical justification for the variation of phonon conductivity with temperature. Some theoretical work on these polymers was reported by Dubey² on the basis of Klemen's expressions³. However, no satisfactory agreement for the experimental observations of Scott *et al*¹ was reported.

In the present paper the lattice thermal conductivity of nylon and polyethylene has been analysed at low temperatures by making use of the extended Callaway model⁴. The phonon conductivity is attributed to phonon scattering due to the dangling electrons present in the strainfields of dislocations and stacking faults. Polymers with lattices far from perfect have much lower lattice thermal conductivity because of shorter mean-free path of lattice vibrations especially at low temperatures. In other words, the strong coupling of lattice vibrations gives rise to higher thermal resistance. Consequently, the lattice thermal conductivity of these polymers varies in a manner similar to the specific heat at low temperatures⁵.

We shall now consider how the various scattering mechanisms affect the lattice thermal conductivity. Relaxation time is an important factor in the

expression of phonon conductivity⁶. Of the various events contributing to the relaxation time, the most important scattering mechanisms are: boundary scattering, point-defect scattering, phonon-phonon scattering, impurity-anharmonicity scattering, four-phonon scattering, electron-phonon scattering, resonant scattering, dislocation and stacking fault scattering, etc. The frequency and temperature dependence of these events can be seen in several references elsewhere^{3,4,6}. At low temperatures phonons are the major heat carriers and it is a notable fact that only the low frequency phonons with long wavelengths excite at lower temperatures. Also, the dominating scattering events for low frequency phonons are: boundary scattering, dislocation and stacking fault scattering and point-defect scattering. Since polymers contain a large number of plastic deformations, phonon scattering from static strainfields of dislocation cores and that from stacking faults is extremely important, contributing to the thermal resistance at low temperatures. At low temperatures phonon scattering from internal and external boundaries of crystal is insignificant, because at these temperatures phonons vibrate only in the low frequency mode with shorter mean-free path (this prominently happens in the crystal containing plastic deformations). Thus, the inclusion of phonon scattering from the surroundings of the static strainfields of dislocations and stacking faults becomes obvious and it has been described in the later part of this note in the hope that it would satisfactorily explain the discrepancies between the theoretical curves² and the experimental observations¹.

The lattice thermal conductivity can be expressed as⁴

$$K = (K_B^4 T^3 / 2\pi^2 \hbar^3 v) (I_1^2 / I_2), \quad (1)$$

where

$$I_1 = \int_0^{\theta/T} x^4 e^x (e^x - 1)^{-2} dx, \quad (2a)$$

and

$$I_2 = \int_0^{\theta/T} \tau^{-1} x^4 e^x (e^x - 1)^{-2} dx. \quad (2b)$$

Here K_B is the Boltzmann constant, θ the Debye temperature, v the phonon velocity and τ the combined relaxation time. In the present case τ is given by

$$\tau^{-1} = \tau_d^{-1} + \tau_s^{-1}, \quad (3a)$$

where τ_d and τ_s are relaxation times for the static strainfield dislocation scattering and stacking fault scattering, respectively and are given by

$$\tau_d^{-1} = 6 \times 10^{-2} N_d b^2 \gamma^2, \quad (3b)$$

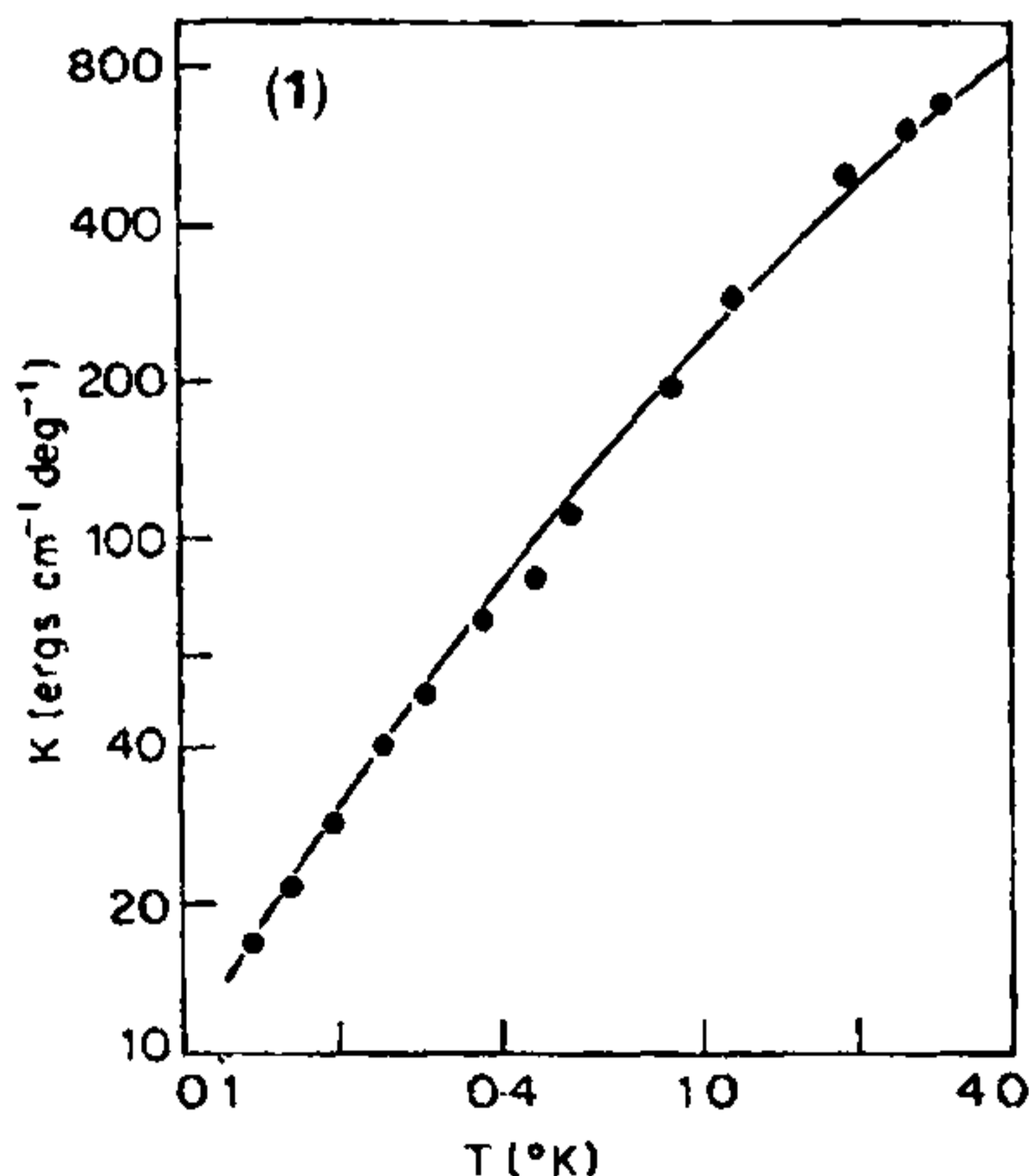
and

$$\tau_s^{-1} = 0.7 (a^2/v) \gamma^2 \omega^2 N_s. \quad (3c)$$

Here N_d and N_s are the numbers of the dislocations and stacking faults per unit area, respectively, γ (≈ 2) the Gruneisen constant b the Burger's vector and a the lattice separation.

Using (2) and (3) in (1) in the low temperature limit ($T \rightarrow 0$, $\theta/T \rightarrow \infty$), we have

$$K = (K_B^4 T^2 / 2\pi^2 \hbar^3 v) \zeta^2(4) [A \zeta(5) + BT \zeta(6)]^{-1}, \quad (4)$$



where

$$A = 6 \times 10^{-2} (b\gamma)^2 K_B N_d / \hbar, \quad (5a)$$

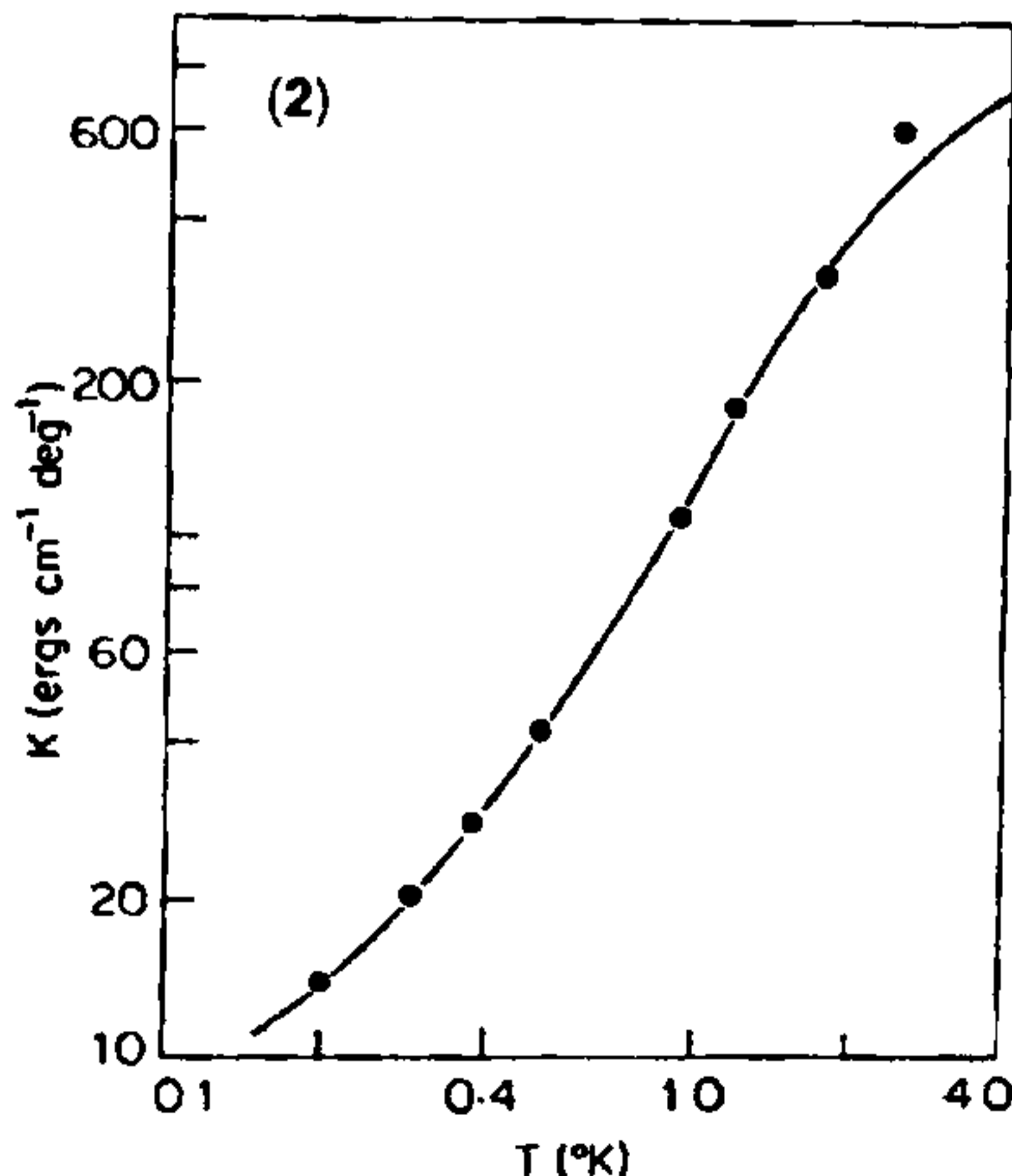
$$B = 0.7 (a\gamma K_B)^2 N_s / V \hbar^2, \quad (5b)$$

and $\zeta(m)$ is the Riemann Zeta function given by

$$\zeta(m) = \int_0^{\infty} x^m e^x (e^x - 1)^{-2} dx, \quad m=4,5,6. \quad (6)$$

The experimental results of Scott *et al* have been used to analyse the lattice thermal conductivity of nylon and polyethylene. Due to lack of data on polymers the values of A and B have been taken as the parameter. In the case of nylon, these are: $A=1.513$, $B=8.8997$ and $v=1.79 \times 10^5$ cm/s, while in the case of polyethylene $A=0.549$, $B=1.195$ and $v=2 \times 10^5$ cm/s.

In calculating the lattice thermal conductivity, the effect of phonon scattering from the surroundings of the dislocation strainfields and stacking faults is found to gradually decrease with increase of temperature, but the contribution due to the stacking faults decreases more rapidly than that due to dislocations. Below 1 K strainfield the scattering imparts an appreciable role and is rather effective than the other scattering processes. While analysing the thermal conductivity of polyethylene it is found that the contribution due to the strainfield scattering



Figures 1 and 2. Phonon conductivity of nylon (1) and polyethylene (2) at low temperature. Solid circles are the experimental points.

is dominant below 1 K but above 1 K it falls more rapidly than that in the case of nylon. The theoretical fits of thermal conductivity curves of nylon and polyethylene (figures 1 and 2) show fairly good agreement with the experimental values.

This procedure of explaining the peculiar behaviour of thermal conductivity can also be applied to the amorphous type of solids. In the low temperature limit there exist phonon modes which are localized specially around the dislocation cores and their frequencies range from zero to ω_0 , where ω_0 is always less than the Debye frequency. These quasi-localized modes are responsible for strainfield and stacking fault scattering of phonons.

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ANNOUNCEMENT

BRAIN STORMING SESSION ON INDIAN SCIENCE AND TECHNOLOGICAL JOURNALS

The above meeting on the issue of Science and Technology Journals in India is aimed at bringing together the concerned persons from various groups for a dialogue where they can arrive at an understanding of the nature of the problem and also examine the points of view of one another. Such a dialogue, it is hoped, would enable us to evolve ways and means of improving the all-round quality of the Science and Technology Journals. The meeting is aimed at taking stock of the situation concerning the Science and Technology activity in this country as a whole.

The meeting is organised by PPST Foundation

and Indian Institute of Technology, Madras with the support from the Department of Science and Technology and Department of Scientific and Industrial Research, Government of India. The meeting will be held at the Indian Institute of Technology, Madras during 17th and 18th March, 1989.

Further particulars may be had from: Dr B. Viswanathan, Secretary, Brain Storming Session on Indian Science and Technology Journals, Department of Chemistry, Indian Institute of Technology, Madras 600 036.