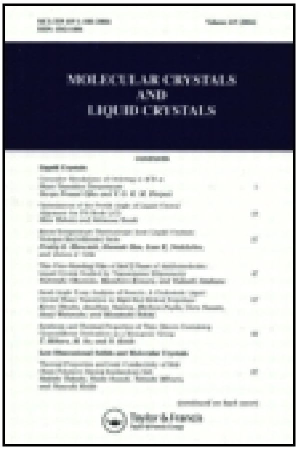

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Thermal Wave Method in Calorimetry

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THERMAL WAVE METHOD IN CALORIMETRY

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Abstract - We have studied the properties of thermal wave propagated along the needle like samples in order to evaluate the specific heat and thermal conductivity.

We confine our attention to the problem of the diffusion of heat in the samples of low thermal diffusivity as organic conductors like to be. The most common assumption related to the standard calorimetric geometry is the uniformity of the temperature within the sample, no matter how rapid is the variation of the heating power on its surface. This may be useful only to some extent if we deal with the samples of a good thermal conductivity. Such materials are ordinary metals and the specimens may be considered as isothermal bodies with the internal thermal resistances to be short circuited.

Organic chain conductors (typical conductivity of the order of 1 $Wm^{-1}K^{-1}$) are far away from this ideal situation, and the interior of the sample must be imagined as a network of distributed thermal capacitances and resistances. This results in the coupling of the measured heat capacity to thermal resistance since it is not possible to separate both quantities starting simply from the temperature response of the sample[1].

We need therefore more consistent study of the propagation of thermal wave in the sample subjected to the heating on one side. For simplicity it will be convenient to suppose that the needlelike sample is heated on one end and another end is thermally grounded to the heat sink (Fig.1).

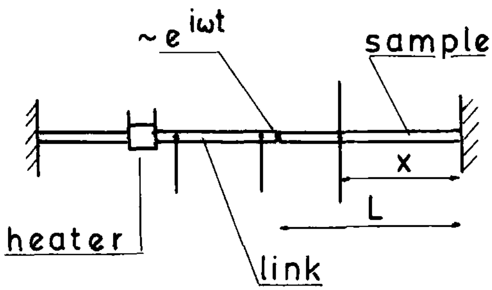

FIG.1 Specimen geometry

Thermal wave propagated along the sample may be considered by the use of the diffusivity equation

$$\delta T/\delta t = \lambda \delta^2 T/\delta x^2 \qquad 1)$$

The solution of this equation is considered in simple form.

$$T(x,t) = A(e^{ikx} - e^{-ikx})\, e^{i\omega t} \qquad 2)$$

The boundary conditions are taken properly

$$T=0 \text{ at } x=0, \quad T = T_0 e^{i\omega t} \text{ at } x=L$$

By the substitution of above solution in Eq.1, one obtains for A

$$A = T/\left[\exp(i-1)\sqrt{\frac{\omega\alpha}{2}}\,L - \exp(i-1)\sqrt{\frac{\omega\alpha}{2}}\,L\right] \qquad 3)$$

It is evident that the phase of thermal wave is dependent upon the position of the probe on the sample (L-x)

$$\Delta\varphi = \sqrt{\frac{\omega\alpha}{2}}\,(L - x) \qquad 4)$$

For fixed ω and x the measurement of $\Delta\varphi$ leads to the thermal diffusivity $\alpha = \rho c/\kappa$. In order to evaluate the specific heat c_p the temperature response is measured at low frequency $\omega \rightarrow 0$

$$T(x,t)=x/L \cdot T_0 e^{i\omega t} \qquad 5)$$

The amplitude $x/L \cdot T_0$ is independent on frequency and expression just evaluated corresponds to the simple voltage divider. Thermal current in the sample is calibrated by the use of the known thermal resistance of thermal link.

An another approach to the problem of evaluation of the specific heat is based upon unique dependence of the temperature response amplitude on

$$T(x,t)=\exp(i\omega t)F(\omega\alpha) \qquad 6)$$

$F(\omega\alpha)$ is measured firstly at fixed temperature but varied. Than the frequency is fixed and temperature slightly changed. The corresponding change in $F(\omega\alpha)$ is normalized again on fixed temperature and the change of thermal diffusivity α is simply the change in ω .

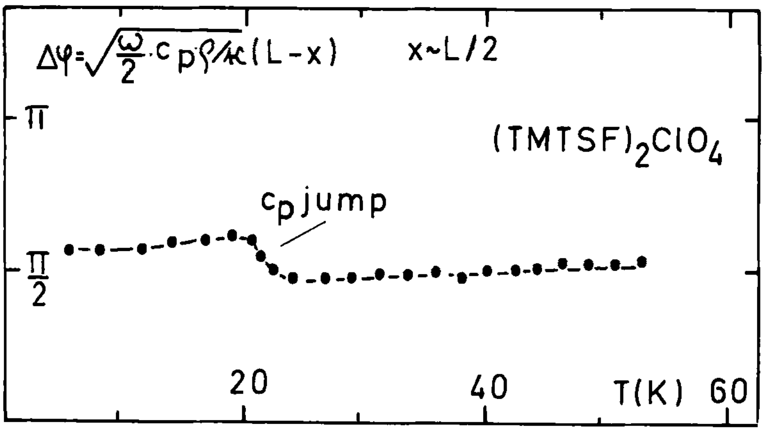

FIG.2 The change of the phase with temperature

By the application of the method just described it is possible to measure the heat capacity and thermal conductivity on the same sample. At low frequency the thermal conductivity is measured explicitely with nor spurious contribution of the heat capacity. At high frequency thermal diffusivity is readly measured.

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