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THERMAL DIFFUSIVITY MEASUREMENTS FOR THIN FILMS BY THE PHOTOACOUSTIC EFFECT

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ABSTRACT

When the thermal diffusivity of materials is measured by using the photoacoustic effect method, a sound wave interference effect will inevitably occur. This interference effect causes an extra phase lag between the modulated light and the sound signal detected with a microphone. A theoretical expression has been developed to relate the phase lag caused by the sound interference effect to the modulation frequency of the incident light. Simulation results of the theoretical expression show good agreement with the experimental results. In some cases, it is convenient to use a reference film to revise the measured results. Furthermore, some theoretical relations between the phase lag and the chopping frequency as well as the thermal diffusivity of a sample have been recast according to the Rosencwaig-Gersho theory.

INTRODUCTION

Two kinds of methods have been used to determine the thermal diffusivity of materials experimentally. One is a method using transient heat flow [1] and the other is a method using periodic heat flow [2]. The measurement of the thermal diffusivity or thermal conductivity of thin films by conventional methods is problematic. However, there is a unique method, a modification of the photoacoustic effect, which was demonstrated for the first time by Adams and Kirkbright [3]. This photoacoustic effect method is a method using periodic heat flow.

The photoacoustic effect has been developed as a useful tool for the spectroscopic study of solids since the Rosencwaig-Gersho [4] theory was established in 1976. A photoacoustic spectrometer consists basically of a chopped light source, a sealed cell and a sound signal detector. The sample absorbs the chopped light and converts it into a periodic heat flow. The periodic heat flow will travel to the surface of the sample and spread into the surrounding boundary gas layer. Therefore, a sound signal is produced in the cell. The sound is detected by means of a sensitive capacitor

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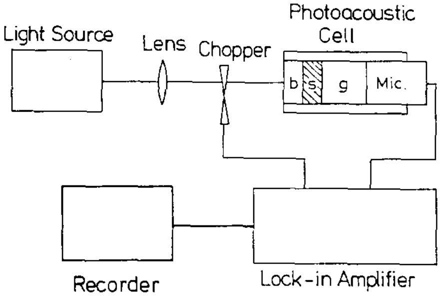

Fig. 1. Experimental set-up of the photoacoustic measurements.

microphone. However, it takes a little time for the heat flow to travel from the front surface to the rear surface of the sample, so that a phase shift will be produced between the chopped light and the sound signal. The phase shift depends on the thermal diffusivity and the thickness of the sample. The measurement of the thermal diffusivity of thin films by the photoacoustic effect utilizes this phase shift [5–7].

In this paper, we deal with the application of the photoacoustic effect to the measurement of the thermal diffusivity of thin films, and we discuss briefly the effect of sound wave interference arising in a photoacoustic effect cell.

EXPERIMENTAL

The arrangement of the experimental set-up developed in our laboratory is shown schematically in Fig. 1. A 30 W halogen lamp was used as the light source. A variable-speed mechanical chopper whose chopping frequency can be varied from 10 to 1000 Hz was used to modulate the incident light. A cylindrical brass cell of diameter 12.7 mm (0.5 in) was fitted with a sensitive 0.5 in capacitor microphone (Bruel and Kjaer type 4166) to detect the sound signal. The distance from the sample to the microphone was about 40 mm. The phase lag between the modulated light and the sound signal was detected with a lock-in amplifier (PAR type 5201).

Thin copper film samples of diameter about 10 mm were used in this study. The bright surfaces of the films were oxidized to make them black in order to increase the light absorption. Some blackened polyethylene films were also used in the experiments. All the samples were completely opaque.

RESULTS AND DISCUSSION

In this paper, the sample surface irradiated by the chopped light will be called the front surface and the other surface will be called the rear surface.

Two kinds of experimental methods are available for photoacoustic measurements, the front-surface method and the rear-surface method, depending on which surface is the source of sound detected by the microphone. As illustrated in Fig. 1, the method used in this study is of the rear-surface kind. With a completely opaque sample, the front surface absorbs all the chopped light and converts it into a heat flow. Adams and Kirkbright [3] have shown the temperature variation at any position within the dimension of the thickness by solving Fourier's thermal diffusion equation. However, the Rosencweig and Gersho theory of the photoacoustic effect, which has been confirmed by another calculation [8], is more precise in expressing the temperature variation in a sample. In the case of the rear-surface method, the temperature variation at the rear surface can be given as

$$\phi(t) = W_0 + W \exp(+j\omega t) \tag{1}$$

where $\phi(t)$ is the complex-valued temperature at the rear surface, W_0 and W are respectively the real-valued and complex-valued constants relative to time t, ω is the frequency of the chopper and j is $(-1)^{1/2}$.

The complex value W can be written as

$$W = \left[\left(\frac{1-g}{1+g}\right) \exp(-2\sigma_s l) E \exp(-\beta l)\left(1 - \frac{\beta}{\sigma_s}\right) + 2\exp(-\sigma_s l) E \left(\frac{g + \beta/\sigma_s}{1+g}\right) - E \exp(-\beta l)(1 + \beta/\sigma_s)\right] \times \left[1 + b - \frac{(1-b)(1-g)}{1+g} \exp(-2\sigma_s l)\right]^{-1} \tag{2}$$

where

$$E = \frac{\beta I_0}{2k_s(\beta^2 - \sigma_s^2)} \tag{3}$$

$$b = \frac{k_b a_b}{k_s a_s} \tag{4}$$

$$g = \frac{k_g a_g}{k_s a_s} \tag{5}$$

The parameters in the above equations are defined as follows. σ_s is the complex-valued thermal diffusion coefficient of the sample and equals $(1+j)a_s$ where $a_s = (\omega/2\alpha_s)^{1/2}$, l the thickness of the sample, I_0 the incident monochromatic light flux, β the optical absorption coefficient of the sample, k_i the thermal conductivity of material i and α_i the thermal diffusivity of material i. The subscript i can be s, g and b when referring to the sample, gas and backing material respectively.

The real part of the complex-valued solution $\phi(t)$ of eqn. (1) is the solution of physical interest and represents the temperature variation at the rear surface of the sample. The phase lag between the chopped light and the

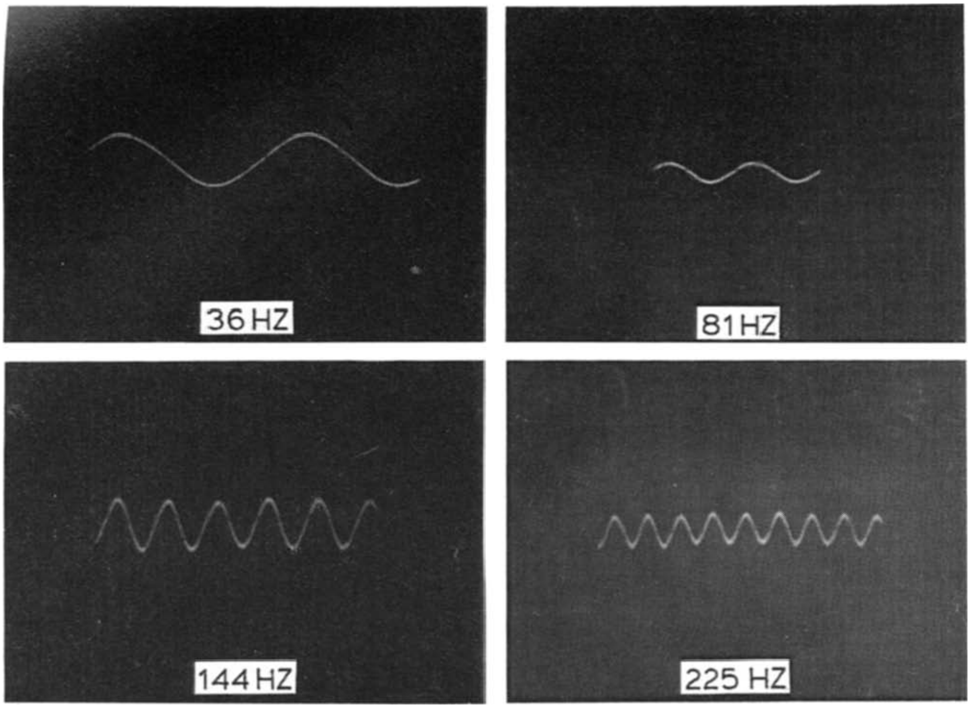

Fig. 2. Representative waveforms of the sound signal for various frequencies.

temperature variation is represented by the angle of the complex value W, whose real part expresses the amplitude of the temperature variation.

Since the ratio of the effusivities of the gas to sample, g, is always less than 1%, it can be neglected in the calculation. In our experiments, the backing material is a gas, so that b is also negligible. Moreover, in the case of an opaque sample ($\sigma_s l \gg 1$), if $\beta \gg \sigma_s$, eqn. (2) is further simplified as follows:

$$W = \frac{I_0}{k_s(1+j)\sigma_s} \frac{\exp(-\sigma_s l)}{[1-\exp(-2\sigma_s l)]} \tag{6}$$

This periodic temperature variation makes the gas layer close to the rear surface of the sample expand and contract periodically. As a result, a sound wave is produced inside the cell. Some representative oscilloscope waveforms of the sound wave detected with a microphone are shown in Fig. 2. All the sound waves with different frequencies have a sine curve shape. Therefore, the phase lag between the modulated light and the temperature variation at the rear surface is given by

$$\Delta\theta = \left(\frac{\omega}{2\alpha_s}\right)^{1/2} l + \tan^{-1}\left\{\frac{\exp\left[-2\left(\frac{\omega}{2\alpha_s}\right)^{1/2} l\right] \sin\left[2\left(\frac{\omega}{2\alpha_s}\right)^{1/2} l\right]}{1-\exp\left[-2\left(\frac{\omega}{2\alpha_s}\right)^{1/2} l\right] \cos\left[2\left(\frac{\omega}{2\alpha_s}\right)^{1/2} l\right]}\right\} + \gamma$$

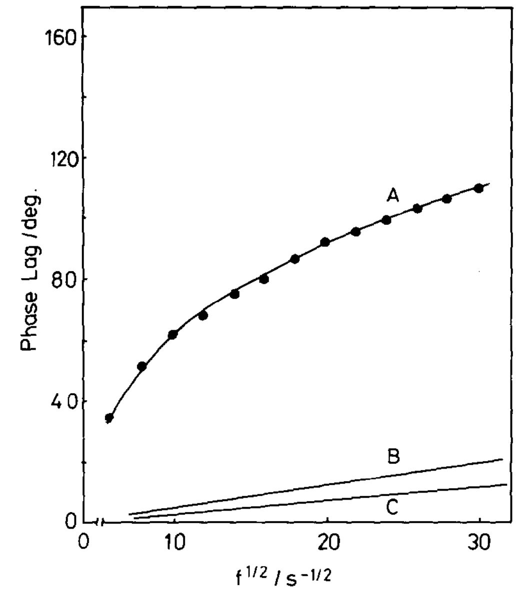

Fig. 3. Plots of the phase lag $\Delta\theta$ vs. $f^{1/2}$ for a copper film of thickness 42 μm: curve A, observed data; curve B, calculated curve from eqn. (7); curve C, calculated curve from eqn. (8).

where γ is a phase lag caused by instrumental characteristics and is a constant. In the case of a thermally thick sample, $\sigma_s l \gg 1$. Hence, the form of eqn. (7) is simplified:

$$\Delta\theta = \left(\frac{\omega}{2\alpha_s}\right)^{1/2} l + \gamma \tag{8}$$

It is evident from eqn. (8) that a graph of $\Delta\theta$ vs. $\omega^{1/2}$ gives a straight line, and that from the slope of the straight line the thermal diffusivity of the sample can be calculated.

Equation (8) represents a special case of eqn. (7) and agrees with the formula reported by Adams and Kirkbright [3]. On the basis of eqn. (8), many successful measurements have been achieved by some researchers.

It is often found for a thermally thin film such as a thin copper film that a plot of $\Delta\theta$ vs. a wide range of $\omega^{1/2}$ is curved over the whole frequency range. It becomes difficult, therefore, to draw a linear line and to obtain the slope. In addition, the measured value of $\Delta\theta$ is considerably greater than theoretically calculated values from eqn. (8). Figure 3 shows the measured result for a copper film 42 μm thick. The chopping frequency was changed in the range from 25 to 1000 Hz. Curve B is the theoretical curve calculated according to eqn. (8) ($\alpha_s = 1.2 \times 10^{-4}$ m^2 s^{-1}) and curve A is the measured curve. A large disagreement is found between these two curves. A similar result has been reported by other researchers [9].

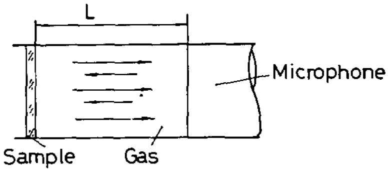

Fig. 4. Cross-sectional view of the photoacoustic effect cell for the explanation of the interference effect.

In the chopping frequency range from 25 to 1000 Hz, $a_s l < 1$. Therefore, the sample under these conditions cannot be assumed to be a thermally thick sample ($a_s l > 1$). This is one reason why a discrepancy appears between the theoretical and experimental curves. For a thermally thin sample, eqn. (7) should be used instead of eqn. (8). Curve B shows the theoretical curve calculated according to eqn. (7). Although curve B gives a better fit to the experimental curve than curve C, considerable disagreement is still retained between curve B and the measured values.

When we measure the phase lag of a thermally thin sample in a wide chopping frequency range, a sound wave interference effect becomes relatively important and even preponderant. This can be considered as the main reason for the disagreement shown in Fig. 3. Figure 4 shows a photoacoustic cell. The distance between the sample and the microphone is L. We assume that the pressure variation is produced only in the gas layer close to the rear surface of the sample. This pressure variation will travel to the microphone as a sound wave at the velocity of sound. The time taken by the sound wave to travel from the gas layer to the microphone causes another phase lag, i.e. a measured phase lag is the sum of the phase lags caused by the thermal diffusion in the sample and by the sound travelling in the cell.

The sound velocity C does not change with chopping frequency, and is assumed to be a constant in experiments. Hence, the time τ required for sound to travel from the rear surface of the sample to the microphone equals

$$\tau = L/c \tag{9}$$

The phase lag caused by the sound wave travelling is proportional to the ratio of the travelling time to the period of the sound wave, which equals the reciprocal number of the chopping frequency:

$$\varphi = \frac{\tau}{(1/f)} 2\pi = 2\pi f L/C \tag{10}$$

where f is the chopping frequency. Furthermore, the sound wave cannot necessarily disappear simultaneously when it impinges on the microphone. The sound wave will be multiply reflected between the microphone and the cell walls until the reflected sound wave is completely damped. What a microphone detects is the superposition effect of all the sound waves. This is said to be the effect of sound wave interference. The sound wave which originally travels to the microphone from the boundary gas layer is called the first sound wave, and a sound wave which travels to the microphone after being reflected once is called the second sound wave etc. Here, we define that a damping coefficient equals the ratio of the amplitude of the $(n+1)$th wave to the amplitude of the nth wave. According to the superposition law of plane sound waves, the phase lag caused by the composite wave of the first wave and all the reflected waves is written as

$$\psi = \varphi + \sum_{n=0}^{\infty} \tan^{-1} \frac{\eta^{2^n} \sin(2^n 2\varphi)}{1 + \eta^{2^n} \cos(2^n 2\varphi)} = \varphi + \tan^{-1} \frac{\eta \sin(2\varphi)}{1 - \eta \cos(2\varphi)} \quad (11)$$

n represents natural numbers from zero to infinity. φ is the factor defined by eqn. (10) and represents the phase lag for the sound wave to travel one way from the sample to the microphone. The first term on the right-hand side of eqn. (11) can be considered to be the phase lag of the first sound wave travelling from the gas layer to the microphone. The second term shows the phase lag relative to the first sound wave caused by the interference effect of the reflected waves.

It is difficult to ascertain the actual damping coefficient of a cell since it includes factors due to the absorption coefficient of cell walls, the damping effect of the gas column in the photoacoustic cell and the sound energy absorbed by a condenser microphone. A simple way to overcome the problem is to calculate the phase lag by computer simulation by assuming a series of values as damping coefficients. Figure 5 shows the result of a mathematical simulation based on eqn. (11). The x axis is the square root of the phase lag of the sound wave on a return trip in a cell, and is proportional to the product of the chopping frequency and the length of the cell. If the length of the cell is known, the x axis becomes proportional to the square root of the chopping frequency. The ordinate is the phase lag of the interference of the sound waves.

When the damping coefficient is zero, i.e. there is no reflected sound wave, then the phase lag will be determined by eqn. (10). The plot of ψ vs. $f^{1/2}$ shows a parabolic curve as depicted in Fig. 5. On increasing the damping coefficient η the phase lag increases abruptly at lower chopping frequencies. If the damping coefficient were equal to unity, sound resonance would occur in the cell. Because a photoacoustic cell is usually very small and is made of metal, a damping coefficient of 0.7–0.9 is quite reasonable.

Using the cell length $L = 40$ mm, the damping coefficient $\eta = 0.88$ and the sound velocity $C = 340$ m s^{-1}, we obtain for the copper film the simulation result shown in Fig. 6. Curve C was calculated according to eqn. (7) and curve B was calculated according to eqn. (11). These two curves represent the phase lags caused by thermal diffusion in the sample and by sound interference in the cell respectively. Curve A is the sum of curves B

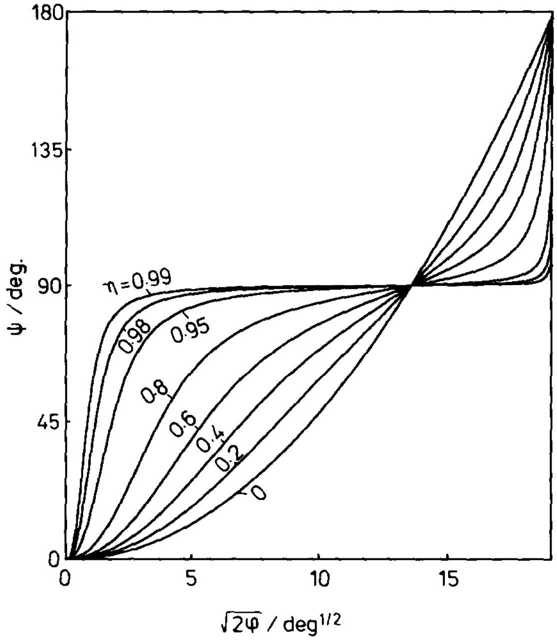

Fig. 5. Theoretical curves of the phase lag ψ caused by sound wave interference as a function of the modulation frequency for various values of η.

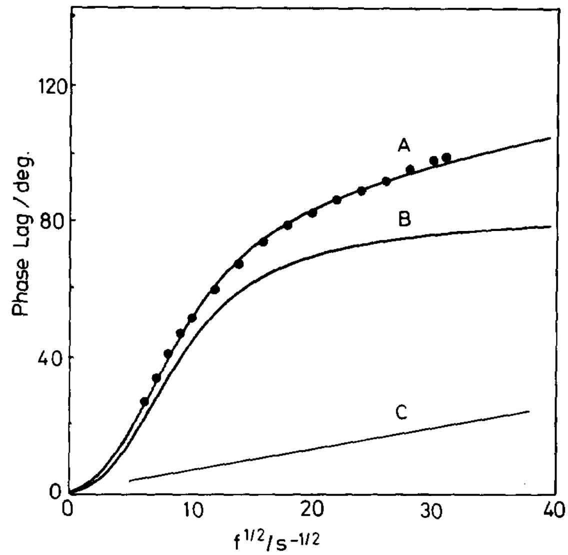

Fig. 6. Replots of the phase lag vs. $f^{1/2}$ for the copper film of thickness 42 μm: curve A, observed data; curve B, phase lag caused by sound wave interference in the cell; curve C, calculated curve from eqn. (7).

and C, and is in good agreement with the experimental plots. This provides evidence that sound wave interference should be taken into consideration.

For a thermally thick film, the effect of the sound wave interference is negligible in a sufficiently high chopping frequency region. However, for a thermally thin film, in general, the measured phase lag includes the phase lag caused by the interference effect. Because ψ is also a function of the chopping frequency, it is necessary to deduct from the measured data the phase lag caused by sound wave interference in order to extract useful information concerning the thermal diffusivity of samples. If a thermally thin sample is used as a reference sample, the difference between the measured phase lags of a sample and the reference will contain only the data concerning the thermal diffusivity and thickness of the sample and reference.

$$\Delta\phi_s - \Delta\phi_r = (\Delta\theta)_s - (\Delta\theta)_r \tag{12}$$

where $\Delta\phi_s$ and $\Delta\phi_r$ are the measured phase lags of the sample and the reference respectively; $(\Delta\theta)_s$ and $(\Delta\theta)_r$ are the phase lags due to thermal diffusions of the sample and the reference respectively. Values of $\Delta\theta$ can be calculated according to eqn. (7) or eqn. (8).

When the reference sample is thermally thin enough compared with the sample, the second term on the right-hand side of eqn. (11) becomes negligible. Especially for a thermally thick sample, eqn. (12) can be rewritten as follows:

$$\Delta\phi_s - \Delta\phi_r = \left(\frac{\omega}{2\alpha_s}\right)^{1/2} l_s \tag{13}$$

Figure 7 shows the results for two copper films; one is 10 μm thick and the other is 62 μm thick. The plots for the two samples are all curved over

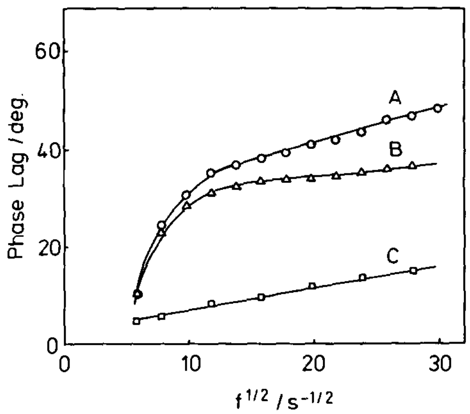

Fig. 7. Dependence of sample thickness on phase lag for copper films: curve A, 62 μm; curve B, 10 μm; curve C, the difference between curves A and B.

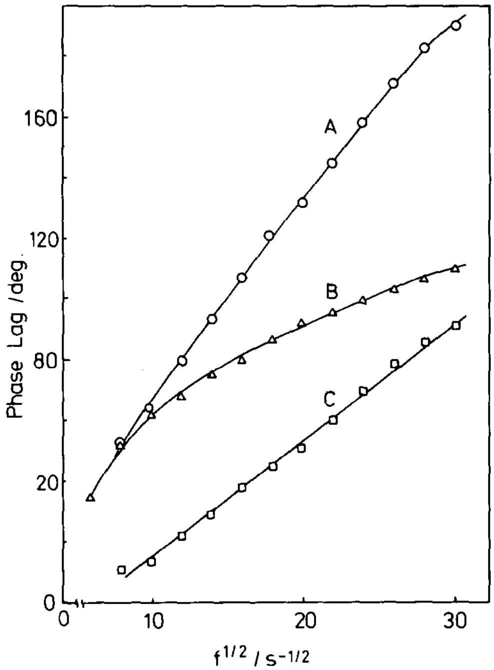

Fig. 8. Plots of phase lag versus $f^{1/2}$ for a polyethylene film: curve A, observed data; curve B, reference data of the thin copper film; curve C, the difference between curves A and B.

the chopping frequency range examined. However, a diagram showing the difference between the two measured curves can be approximated by a straight line over the whole chopping frequency range. Therefore, the thermal diffusivity of copper can be determined from the slope of the line. The value obtained for the thermal diffusivity equals 1.3×10^{-4} m^2 s^{-1}, which shows good agreement with the reported data of 1.2×10^{-4} m^2 s^{-1} [10]. On the other hand, by using a black copper film 42 μm thick as a reference sample, the phase lag measurements for a blackened polyethylene film 96 μm thick were carried out. The result is shown in Fig. 8. The thermal diffusivity measured in this way is 4.8×10^{-6} m^2 s^{-1}, which is reasonable in comparison with the reported value [11].

CONCLUSION

The thermal diffusivity of thin films was investigated by employing the photoacoustic effect method. It has been shown in this paper that for a thermally thin sample, the relationship between the modulation frequency of incident light and the detected sound signal changes in a more complicated manner than that reported by Adams and Kirkbright. This is caused by the sound wave interference effect in a photoacoustic cell. A correction for the measured phase lag can be made in some cases by using a reference sample. In this correction method, the phase lag for thermally thin films such as a copper film of several micrometers thickness can be determined precisely. The simulation of sound wave interference has been performed. The result of the simulation shows good agreement with the experimental result.

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