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A Refined Analysis Procedure for Low Temperature Transient Thermal Measurements[1]

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We have employed a heat-pulse technique to study thermal properties at low temperatures. In the course of these studies we have identified a number of significant aspects of thermal transients which are not normally taken into account. These include finite-time effects for thermal diffusion, a modified equation in the presence of boundary scattering, and the role of thermal boundary resistance at the sample holder. We have used a steady-state, two-heater thermal conductivity measurement in conjunction with the heat-pulse studies to elucidate the latter effect. The result is that pulse measurements using a single thermometer can be used to determine both the boundary resistance *and* the heat capacity and thermal conductivity of a sample.

KEY WORDS: heat capacity; low temperature; thermal diffusivity; transient technique.

1. INTRODUCTION

We have employed a heat-pulse technique to study thermal properties at low temperatures. This technique, which allows simultaneous determination of the heat capacity and thermal diffusivity, has the potential for measuring extremely small heat capacities as in thin films. The advantages of this technique, together with corrections for addenda and methods for data analysis, have been discussed in a previous paper [1]. Here we describe additional aspects and subtleties not covered before. These corrections are quite general in nature and should be applicable to other transient techniques. In particular, we provide closed-form solutions to the dif-

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fusion equation for the case of imperfect thermal contact at the sample holder and for the case of finite propagation velocity. The consequences of ignoring these and other factors in heat-pulse experiments are examined.

Our method involves the introduction of a heat pulse at the free end of a long sample which is clamped to a temperature-controlled flange. The temperature is monitored at a distance x from the heater using a superconducting thin-film bolometer. The recorded temperature profile as a function of time is compared to the solution of the one-dimensional diffusion equation with appropriate boundary conditions. The two fitting parameters are the heat capacity per unit volume, C, and the thermal diffusivity, D.

The temperature profiles can conveniently be broken into early and late time segments relative to the time of the temperature maximum, $t_{\max}(\approx x^2/2D)$. This paper is concerned primarily with important correction factors which affect the response of the system in these respective time segments. In Section 2 we provide the solution to the ordinary diffusion equation and discuss previous data analyses based on that solution. Section 3 deals with corrections to early-time data which involve finite propagation time effects (causality) and boundary scattering. Section 4 examines late-time data, the effects of boundary resistance at the clamp, and the consequences of ignoring "small" terms in the fitting routine. Finally, Section 5 summarizes the effects of these considerations on thermal-property measurements.

2. PREVIOUS FITTING TECHNIQUES

2.1. Acausal (Instantaneous Response) Solution with No Thermal Boundary Resistance

For our geometry, the parameters are the heat input Q, sample length L, cross-sectional area A, and bolometer location x measured relative to the free end of the sample. Assuming perfect thermal contact at the clamped end, the solution to the ordinary diffusion equation

$$\dot{T} = D\nabla^2 T \tag{1}$$

can be written

$$\delta T = (2Q/LCA) \sum_{n=1,3,5,\ldots} \exp(-D\pi^2 n^2 t/4L^2) \cos(n\pi x/2L) \tag{2}$$

or, equivalently, as

$$\delta T = (Q/CA\sqrt{\pi D t}) \exp(-x^2/4Dt) \left\{ 1 + \sum_{-\infty}^{\infty} (-1)^n \times \exp[-n^2 L^2 (1 - x/nL)/Dt] \right\} \tag{3}$$

These two solutions form convenient starting points for analyzing late- and early-time data, respectively.

2.2. Early-Time Data

For times $t < t_{\max}$, and provided that $x < L/2$, the contribution of the infinite series in Eq. (3) is negligible and the solution reduces to the semi-infinite sample result:

$$\delta T = (Q/AC\sqrt{\pi D t})\exp(-x^2/4Dt) \tag{4}$$

A plot of $\ln(\delta T\sqrt{t})$ against $1/t$, then, should give a straight line with the slope determined by the diffusivity D and the intercept determined by the specific heat C. This approach was used by Bertman et al. [2], who observed the expected linear behavior except at late times.

2.3. Late-Time Data

The usual approach is to fit the data for times $t > 2t_{\max}$ to a single exponential. This seems justified because the contribution of the second term in Eq. (2) is only a few percent of the first term. Consequently, in a plot of $\ln(\delta T)$ against t, the slope and intercept will be determined by D and C, respectively.

2.4. Moments

An alternative approach to analysis is to use all of the data to calculate various temperature moments [3]:

$$f_n = \int_0^{\infty} \delta T\, t^n\, dt \tag{5}$$

By taking ratios of appropriate moments, C and D can be determined. This method actually incorporates the two previous techniques since the early data are usually obscured by electrical pickup and must be reconstructed to calculate the moments. Similarly, the very late-time data must be extrapolated from earlier points using Eq. (2) since the temperature response is obscured by noise at late times. Because the moments are calculated in practice by using the previously discussed fitting routines, any corrections to these fits will also affect the moments method.

3. Early-Time Corrections

3.1. Causality

The ordinary diffusion equation [Eq. (1)] is acausal in that it predicts an immediate response at the bolometer when the heater is energized [Eqs. (2) and (3)]. In actuality, there must be a minimum time for the heat to diffuse to the bolometer. This time will be given roughly by x/v, where v is a carrier velocity. For phonon carriers in our geometry, the minimum time is of the order of $1\,\mu s$ and cannot be neglected.

To account for the finite-time effect, some authors have incorporated an additional term in the diffusion equation [4]:

$$\tau \ddot{T} + \dot{T} = D\nabla^2 T \tag{6}$$

where τ is a characteristic carrier relaxation time. For a semiinfinite sample, an appropriate early-time solution of the modified equation is [5]

$$\delta T = (Qv/ACD)\exp(-v^2 t/2D)\, J_0[(v/2D)\sqrt{x^2 - v^2 t^2}]\, u(t - x/v) \tag{7}$$

where now $v = \sqrt{D/\tau}$.

If we introduce the retarded time $t' = t - x/v$ and expand the Bessel function, Eq. (7) reduces to

$$\delta T = (Q/AC\sqrt{\pi D t'})\exp[-(v^2 t'/4D)(\sqrt{1 + 2x/vt'} - 1)^2](1 + 2x/vt')^{-\frac{1}{4}} \tag{8}$$

It can be readily verified that one recovers the acausal solution in the limit of infinite v.

To examine the effects of the finite propagation velocity, we first show a plot of the expected temperature response for both infinite and finite v (Fig. 1), choosing reasonable values for the other required parameters. These computer-generated data were then fit using the conventional scheme given in Section 2.2, which ignores the causality effect. The numerical results are shown in the Fig. 1. Except for very early times, even the causal plot looks quite linear. However, the error in D is nearly 5%, while that of the calculated C is about 2%.

Since these errors are small, the effect can easily be overlooked, especially if a longer time scale is employed when obtaining the data. The important point here is that a more sophisticated fitting routine based on Eq. (6) not only would give more accurate results for D and C, but also would allow one to determine the propagation velocity of the pulse. This parameter is of considerable interest but has not previously been determined in this way.

3.2. Matthews' Equation

The essential physics of the diffusion equation is altered considerably when boundary scattering dominates. The effects should be most apparent in crystalline materials at low temperatures when the intrinsic mean free path becomes larger than the sample dimensions.

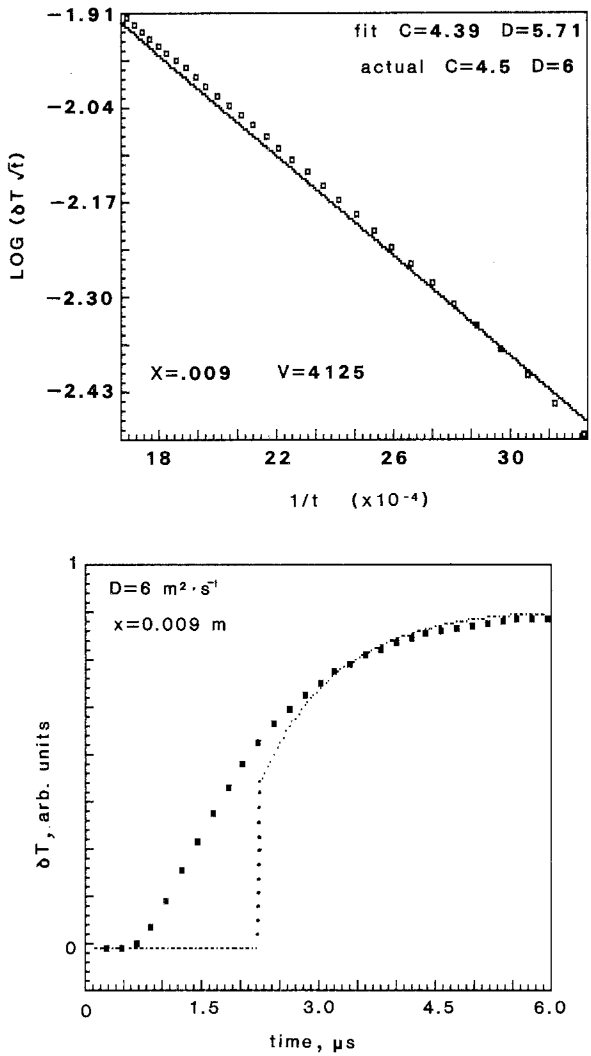

Fig. 1. Calculated temperature response for finite and infinite pulse velocity (bottom). Results of fitting finite velocity data to Eq. (4), which assumes an infinite velocity (top).

Matthews' analysis of this problem [6] for phonons in cylindrical geometry has led to the following diffusion equation:

$$\dot{T} = D\nabla^2 T - A\nabla^2 \dot{T} \tag{9}$$

where $D = \bar{c}I_1 a/2\pi^2$ and $A = \alpha I_2 a/2\pi^2$. Here $\bar{c}$ is the Casimir average velocity of the phonon modes $[\overline{(1/c_i^2)}/\overline{(1/c_i^3)}]$, a is the sample radius, and $\alpha[= \bar{c}\overline{(1/c_i)}]$ is a numerical factor of order unity. The factors I_1 and I_2 are dimensionless integrals in which the finite length of the sample is taken into account. A potential complicating factor which is not included is specular reflection.

Unfortunately, Eq. (9) is valid only for long-wavelength components of T. This restriction has hampered our attempts to obtain an analytic solution for our geometry. The situation is further complicated if, as we believe, the "causality" term of Eq. (6) must be included in Eq. (9). The effect of either additional term (or both) is to prevent the bolometer response from starting immediately after the heater has been energized.

We have made extensive measurements on crystalline sapphire substrates for which the early-time data are not described by conventional diffusion as in Section 2.2. If the data are forced into the form of Eq. (4), a "best fit" is consistently obtained by inserting a time delay of 1 or 2μs. This is clear evidence that the effects we have described are important and measurable in our experiments. A more complete analysis and comparison with actual data will be published elsewhere. To our knowledge there has been no previous experimental verification of Eq. (9) using direct transient techniques.

4. LATE-TIME CORRECTIONS

4.1. Validity of Single-Exponential Fits

As mentioned previously, the standard procedure for fitting late-time data has been to fit to a single exponential for times greater than $2t_{\max}$. The contributions of the second term in the series of Eq. (2) are typically about 4% at $2t_{\max}$ and 1.6% at $3t_{\max}$, respectively. Because the corrections are small, a semilogarithmic plot appears linear over this time scale as shown in Fig. 2. Nevertheless, a single exponential fit will lead to errors of greater than 10% for D and greater than 5% for C under these conditions! It is necessary to incorporate at least two of the exponential terms to obtain acceptable results.

We have used an iterative routine which enables us to fit to the first three exponential terms. This method exploits the fact that the con-

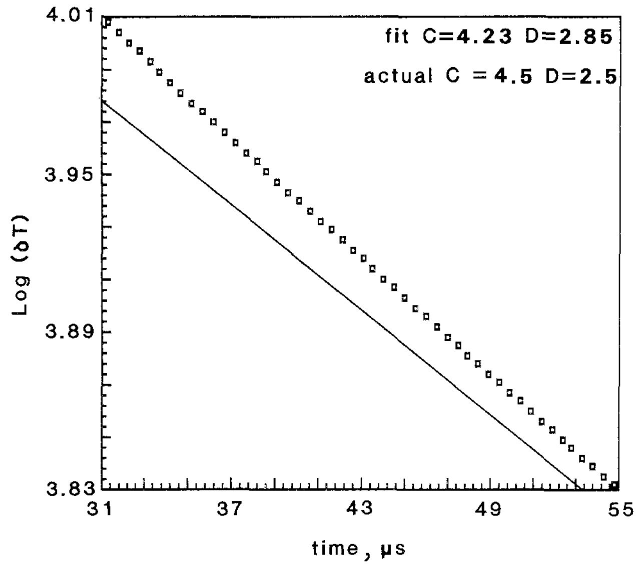

Fig. 2. Fit of data generated from Eq. (2) to a single exponential term from $2t_{max}$ to $3.5t_{max}$. The solid line shows the expected result.

tributions of succeeding terms in the series are small compared to the first term. The procedure requires a reasonable first estimate of the factor $\gamma = D\pi^2/4L^2$. The estimated value is used in a fitting routine which then returns a new value, γ', and iteration is continued until the fit converges.

For the case of zero boundary resistance (see Section 4.2), the relevant equations are as follows:

$$\text{ordinate,} \quad y = \ln[\delta T/(1+\varepsilon)]; \qquad \text{abcissa,} \quad x = t \tag{10}$$

where

$$\varepsilon = \frac{\cos(3\pi x/2L)\exp(-8\gamma t) + \cos(5\pi x/2L)\exp(-24\gamma t)}{\cos(\pi x/2L)} \tag{11}$$

The slope then is equal to $-\gamma'$ and the intercept gives $\ln[(2Q/ACL)\cos(\pi x/2L)]$. This technique is generally applicable whenever succeeding terms in a series solution are known and are small compared to the first term.

4.2. Boundary Resistance at the Clamp

If one tries to avoid the complications of fitting to a sum of exponentials by going to even later times, another problem enters. As very late-time data are used, the effect of boundary resistance becomes paramount. This may be modeled by replacing the usual boundary condition, $T=0$ at $x=L$, by the condition $k(\partial\delta T/\partial x) = -h\delta T$. Here k is the thermal conductivity of the sample and h is the thermal boundary conductance [7]. The consequent solution to the ordinary diffusion equation becomes

$$\delta T = (2Q/AC) \sum_{n=1}^{\infty} g_n(x+L)\, g_n(L) \exp(-D\alpha_n{}^2 t)/R_n \tag{12}$$

where

$$g_n = k\alpha_n \cos(\alpha_n x) + h \sin(\alpha_n x)$$

$$R_n = L(k^2\alpha_n{}^2 + h^2) + kh$$

and

$$\tan(2\alpha_n L) = (2\alpha_n kh)/(k^2\alpha_n{}^2 - h^2)$$

While the sum is over all n, the coefficients for even values of n are typically five orders of magnitude smaller than the odd coefficients and can be neglected.[3]

In Fig. 3 we show computer-generated data for several values of the parameter hL/k. Note that, as hL/k becomes large, the solutions approach

[3] Subsequent investigation has shown that the even coefficients are zero.

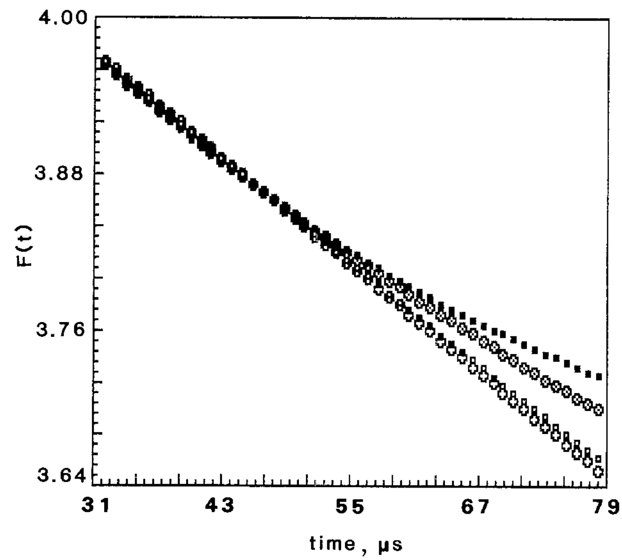

Fig. 3. Fit of data generated from Eq. (12), which includes boundary resistance at the clamp, to Eq. (2), which ignores it. The fit uses the routine described in section 4.1, where $F(t) = \ln[T/(1+\varepsilon)]$. The values of hL/k used are (■) 0.3, (⚙) 3, (□) 30, and (✿) 300.

the prediction of Eq. (2), but only slowly. Only for $hL/k > 500$ do the results on this time scale agree with the perfect-contact model.

To emphasize the importance of this correction, we have calculated the theoretical boundary resistance for a sapphire sample clamped to a copper holder [8]. At low temperatures, the theoretical ratio h/k is $\approx 930\ \mathrm{m}^{-1}$! Thus, sample lengths in excess of 0.5 m would be required in order to neglect the corrections for ordinary measuring times. We have made direct measurements of h/k for the sapphire/copper combination using a two-heater [9], steady-state technique. Even with various clamping arrangements, greases, and the like, we have been able to achieve only about one-tenth of the ideal boundary conductance. The consequent corrections for very late-time data analysis are considerable. In practice, we incorporate hL/k as a third fitting parameter and use a multiterm exponential fit as described in Section 4.1. As a corollary to this work, early-time data, late-time data, and single-heater steady-state measurements may be analyzed together for self-consistent values of the three parameters D, C, and hL/k.

5. CONCLUSIONS

We have shown that previous data analysis techniques for transient thermal measurements can result in significant errors. Boundary resistance is a potential problem in any geometry where heat is transported between dissimilar materials. One must be extremely careful when neglecting exponentially small terms in series solutions to the diffusion equation. Finally, early-time data can be misleading if causality and the effects of boundary scattering are not carefully considered. The latter topics are of fundamental interest and will be treated more extensively in later publications.

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