Implications of a nonlinearity in the theory of second sound in solids

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The phenomenological relations usually employed to describe second sound in pure nonmetallic solids at temperatures θ near that at which the thermal conductivity attains its maximum value were recently found to imply a quadratic dependence of the internal energy density e on the magnitude of the heat flux q, i.e., $e=e_0(\theta)+a(\theta)q^2$. The coefficient $a(\theta)$ can be calculated from measurements of the temperature dependence of the speed $\hat{U}(\theta)$ of second-sound pulses in media for which the unperturbed temperature field is uniform. The studies of second-sound pulses in NaF crystals by Jackson, Walker, and McNelly and in Bi crystals by Narayanamurti and Dynes yield $a(\theta)>0$ and $da(\theta)/d\theta<0$. The theory of pulse propagation along temperature gradients is examined here in detail. For $a(\theta)>0$ the theory implies that a small pulse propagating in a body conducting heat will travel more slowly in the direction of heat flow than in the opposite direction. The magnitude of the effect is estimated for NaF and Bi crystals.

I. INTRODUCTION

In a unidimensional flow of heat with the heat flux q, the temperature θ, and the internal energy density e functions of x and t, if the accompanying deformation is not appreciable, balance of energy yields

$$e_t+q_x=0 , \tag{1}$$

where the subscripts indicate partial derivatives with respect to t and x. Material behavior is described by constitutive equations relating q and e to the temperature field. In Fourier's theory,

$$q=-\kappa(\theta)\theta_x \tag{2}$$

and

$$e=e_0(\theta),\ \text{i.e.,}\ e_t=c_0(\theta)\theta_t , \tag{3}$$

with $c_0=e_0'(\theta)>0$ the heat capacity per unit volume and $\kappa(\theta)>0$ the thermal conductivity. (The prime here indicates the derivative of a function of a single real variable.) The system of partial differential equations governing the evolution of q and θ in the classical theory is

$$\begin{aligned} &q+\kappa(\theta)\theta_x=0 ,\\ &q_x+c_0(\theta)\theta_t=0 . \end{aligned} \tag{4}$$

When κ and c_0 are independent of θ, this system yields the familiar linear parabolic equation, $c_0\theta_t=\kappa\theta_{xx}$ for $\theta=\theta(x,t)$.

It is often observed that Cattaneo's equation,

$$\tau(\theta)q_t+q=-\kappa(\theta)\theta_x , \tag{5}$$

with $\tau(\theta)>0$, supplies a generalization of Eq. (2) that yields field equations which, because they are hyperbolic, are free from the "paradox of instantaneous propagation."[1] In 1963, Chester[2] suggested Eq. (5) as a model of second sound in nonmetallic crystals with τ set equal to $3\kappa V^{-2}c_0^{-1}$, where V is the root-mean-square phonon speed.[3–6] At that time second sound had not yet been observed in solids. In 1964, Guyer and Krumhansl[7,8] showed that Eq. (5) with τ the relaxation time for phonon processes that are dissipative because they do not conserve phonon momentum, can hold only when $\tau_N \ll \tau$, where $\tau_N=\tau_N(\theta)$ is the relaxation time for N processes, i.e., phonon-phonon interactions that conserve momentum. If one maintains terms $O(\tau_N)$, Guyer and Krumhansl's use of the linearized Boltzmann equation for phonons in the Debye approximation yields the relation[9]

$$q_t+\tau^{-1}q+\tfrac{1}{3}c_0V^2\theta_x=\tfrac{9}{5}\tau_N V^2 q_{xx} , \tag{6}$$

which reduces to Eq. (5) with $\kappa=\frac{1}{3}\tau c_0 V^2$ in the limit of small values of $(\kappa\tau_N/c_0\tau)q_{xx}$.

Heat-pulse experiments have shown that second sound can propagate in high-purity crystals of the following substances: ^{4}He,[10] ^{3}He,[11] NaF,[12] and Bi.[13] Equation (6) and equations obtained from it by modifying the coefficient of the term linear in q_{xx} have been used to analyze the shape of the pulses recorded in such experiments.[14–18] A purpose of such analyses has been to obtain information about the dependence of τ_N on θ. For two materials (NaF and Bi) in which the velocity of second-sound pulses has been measured over an appreciable range of temperature,[12,13] it appears that there are intervals of values of θ in which $\tau_N(\theta)/\tau(\theta)$ is sufficiently small that the observed pulses are governed by Eq. (5); in each case the interval contains the value of θ, θ_m, at which $\kappa(\theta)$ attains its maximum value, $\kappa_m=\kappa(\theta_m)$.

The theory we discuss here is based on Eq. (5) and may be called the elementary phenomenological theory of second sound in solids.[19–28] We emphasize that, because the theory can be applied only when the rate of N processes greatly exceeds the rate of dissipative processes, whether they be umklapp phonon-phonon interactions or phonon-defect interactions, it is useful for only a small class of pure crystals, and for them in narrow temperature ranges. Moreover, as has been emphasized by Mikhail and Simons,[29,30] derivations of Eq. (5) [or its extension, Eq. (6)] from the Boltzmann equation rest on an assumption that the relaxation time τ for dissipative phonon processes be independent of the phonon wave number, which suggests that values of τ (and τ_N) obtained from pulse-propagation data may be expected to depend somewhat on the initial pulse shape.[31,32]

Coleman, Fabrizio, and Owen[22–24] have pointed out that the constitutive relation (5) is compatible with the laws of thermodynamics only if the densities of the internal energy e, the entropy η, and the Helmholtz free energy $\psi=e-\theta\eta$ (all per unit of volume) are not functions of θ alone but are instead given by functions $\tilde{e},\tilde{\eta},\tilde{\psi}$ of θ and q with the forms,

$$e=\tilde{e}(\theta,q)=e_0(\theta)+a(\theta)q^2 , \tag{7}$$

$$\eta=\tilde{\eta}(\theta,q)=\eta_0(\theta)+b(\theta)q^2 , \tag{8}$$

$$\psi=\tilde{\psi}(\theta,q)=\psi_0(\theta)+\frac{z(\theta)}{2\theta}q^2 , \tag{9}$$

where

$$z(\theta)=\tau(\theta)/\kappa(\theta) , \tag{10}$$

$$a(\theta)=\frac{z(\theta)}{\theta}-\frac{z'(\theta)}{2} , \tag{11}$$

$$b(\theta)=\frac{z(\theta)}{2\theta^2}-\frac{z'(\theta)}{2\theta} . \tag{12}$$

These functions obey the relations,

$$\tilde{e}_\theta=\theta\tilde{\eta}_\theta,\quad \tilde{\psi}_\theta=-\tilde{\eta} \tag{13}$$

(with $\tilde{e}_\theta=\partial\tilde{e}/\partial\theta$, etc.), which imply the familiar relations $\theta\eta_0'=c_0$, $\psi_0'=-\eta_0$ for the equilibrium functions, ψ_0, η_0, and $c_0=e_0'$.

Equation (7) implies that e_t is not given by the classical formula, $e_t=c_0(\theta)\theta_t$, but instead by

$$e_t=[c_0(\theta)+q^2a'(\theta)]\theta_t+2a(\theta)qq_t , \tag{14}$$

and hence, if one assumes the constitutive relation (5), one is lead to the conclusion that the evolution of q and θ is governed by the system,

$$\begin{aligned} &q+\tau(\theta)q_t+\kappa(\theta)\theta_x=0 , \\ &q_x+c_0(\theta)\theta_t+a'(\theta)q^2\theta_t+2a(\theta)qq_t=0 . \end{aligned} \tag{15}$$

It follows from Eqs. (7)–(13) that on each smooth solution of the system (15) the rate of production of entropy, i.e., the quantity

$$\gamma=\eta_t+(q/\theta)_x , \tag{16}$$

obeys

$$\gamma=q^2/[\kappa(\theta)\theta^2] , \tag{17}$$

and hence vanishes with q and is positive wherever q is not zero.

The *steady-state solutions* of the system (15), i.e., the solutions (θ,q) with $q_t\equiv\theta_t\equiv0$, are the same as those of the classical system (4) based on Eqs. (2) and (3). In fact, a pair (θ,q) is a steady-state solution of (4) and (15), if and only if q is constant in space, i.e., $q(x,t)=q(t)$, in which case both (4) and (15) yield

$$q\equiv q^0\equiv\text{const} , \tag{18}$$

$$\theta_t=0,\quad \theta_x=-\kappa(\theta)^{-1}q^0 . \tag{19}$$

When $q\equiv0$, the solution (θ,q) has the form $(\theta^0,0)$, with θ^0 constant in space and time, and is called an *equilibrium state.*

As κ and τ are both positive, each equilibrium state has a neighborhood in which the system (15) is hyperbolic. Whereas linearization of (4) about an equilibrium state $(\theta^0,0)$ yields a parabolic system that shows instantaneous propagation of disturbances, linearization of (15) about $(\theta^0,0)$ yields the hyperbolic system,

$$\begin{aligned} &q+\tau(\theta^0)q_t+\kappa(\theta^0)\theta_x=0 , \\ &q_x+c_0(\theta^0)\theta_t=0 , \end{aligned} \tag{20}$$

which was put forth by Cattaneo and others,[1,2,33] and for which it is known that the slopes of the characteristic lines, i.e., the characteristic velocities, are $\pm\hat{U}(\theta^0)$ with

$$\begin{aligned}\hat{U}(\theta^0)&=+\left[\frac{\kappa(\theta^0)}{\tau(\theta^0)c_0(\theta^0)}\right]^{1/2}\\ &=+[z(\theta^0)c_0(\theta^0)]^{-1/2} .\end{aligned} \tag{21}$$

The heat-pulse experiments mentioned above yield pulse speeds that can be identified with $\hat{U}$, provided the temperature is such that Eq. (5) holds; for in those experiments the pulse is propagating into an equilibrium state, $(\theta^0,0)$, and, when viewed as a perturbation of $(\theta^0,0)$, the pulse appears weak enough to permit linearization of the system (15).[34]

For the two solids, NaF and Bi, for which there are available pulse speeds as functions of θ,[12,13] values of $z=\tau/\kappa$ can be obtained from Eq. (21) in the temperature interval in which Eq. (5) holds. Once z is known as a function of θ, a in Eq. (7) can be calculated from Eq. (11). The results of such calculations are given in Sec. III; they yield

$$a(\theta)>0 , \tag{22a}$$

$$a'(\theta)<0 . \tag{22b}$$

Because $c_0(\theta)$ is positive, it follows from (22b) and (7) that, for each value of θ, $|q|$ has a critical value

$$q_*(\theta)=+\{c_0(\theta)/[-a'(\theta)]\}^{1/2} , \tag{23}$$

for which

$$\frac{\partial}{\partial\theta}\tilde{e}(\theta,q)\begin{cases}>0, & |q|<q_*(\theta) ,\\ =0, & |q|=q_*(\theta) ,\\ <0, & |q|>q_*(\theta) .\end{cases} \tag{24}$$

It is our present point of view that the constitutive relation (5), and thus Eq. (7) and the system (15), are not applicable to solids when $|q|$ exceeds q_*. We therefore emphasize here cases in which $|q|$, although it has a significant effect on e, is less than q_*.[35]

We study here consequences of the relation (7), with $a(\theta)$ as in (22), for the propagation of heat pulses into media which are not in equilibrium states. In the elementary theory of second sound, the relation (7) implies that the underlying heat flux can influence the speed of a small perturbing pulse; our goal here is to calculate the sign and magnitude of the effect.

II. THE EFFECT OF q ON THE SPEED OF PULSES

The function $\tilde{e}$ of Eq. (7) determines the characteristic curves of the nonlinear system (15). Each real root u of the equation,

$$u^2 z(\theta)\tilde{e}_\theta(\theta,q)+u\tilde{e}_q(\theta,q)=1 , \tag{25}$$

is the slope of a characteristic curve through the point at which θ and q have the values shown.[25] When $q=0$, the solutions of Eq. (25) are $\pm\hat{U}(\theta)$ with $\hat{U}(\theta)$ as in Eq. (21). The relevant cases in which $q\neq 0$ are those in which either (i) $a'(\theta)\geq 0$, or (ii) if $a'(\theta)<0$, then $|q|<q_*$. In such cases we define $U_0(\theta,q)>0$ by

$$U_0(\theta,q)^2=[z(\theta)\tilde{e}_\theta(\theta,q)]^{-1} = \frac{\kappa(\theta)}{\tau(\theta)}[c_0(\theta)+q^2a'(\theta)]^{-1} . \tag{26}$$

When (i) or (ii) holds, the system (15) is hyperbolic, for Eq. (25) then has two distinct roots, u_+ and u_-; these roots are of opposite sign and are given by

$$u_+=U(\theta,q),\quad u_-=-U(\theta,-q) , \tag{27a}$$

where

$$U(\theta,q)=U_0(\theta,q)\{[1+\phi(\theta,q)^2]^{1/2}-\phi(\theta,q)\} \tag{27b}$$

with[36]

$$\phi(\theta,q)=\tfrac{1}{2}U_0(\theta,q)\tilde{e}_q(\theta,q)=U_0(\theta,q)a(\theta)q . \tag{27c}$$

When $a'(\theta)<0$, for $|q|=q_*(\theta)$ the system (15) is parabolic with its single characteristic slope agreeing in sign with q and its magnitude given by $|u| =[2a(\theta)q_*(\theta)]^{-1}$.[37]

Let us now assume, in accord with experience, that (22a) holds for all θ and, in addition, that on the solution (θ,q) under consideration (i) or (ii) holds, so that the system (15) is hyperbolic everywhere at each time. Suppose that (θ,q) is perturbed by a small pulse, i.e., by a disturbance of low amplitude and narrow width. If the perturbing pulse is located at an initial point x_i at time t_i, it will arrive at another, not too distant, point x_r at a time $t_r>t_i$, provided $x_r=\xi(t_r)$, where ξ is the solution of the differential equation,

$$\frac{d\xi}{dt}=u(\xi,t) , \tag{28}$$

with the initial condition $\xi(t_i)=x_i$. In Eq. (28),

$$u(\xi,t)=u_+(\xi,t)=U(\theta(\xi,t),q(\xi,t)),\quad \text{if } x_r>x_i , \tag{29}$$

i.e., if the pulse is traveling to the right, and

$$u(\xi,t)=u_-(\xi,t)=-U(\theta(\xi,t),-q(\xi,t)) ,\quad \text{if } x_r<x_i , \tag{30}$$

i.e., if the pulse is traveling to the left. Thus $u_+=U(\theta,q)$ is the speed with which the influence of a small disturbance propagates in the direction of increasing x, and $-u_-=U(\theta,-q)$ is the speed with which the influence of such a disturbance propagates in the opposite direction. If we write Δu for the amount by which this latter speed exceeds the former, we have, by Eqs. (27) and (26),

$$\begin{aligned}\Delta u&=-u_--u_+=U(\theta,-q)-U(\theta,q)\\&=2U_0(\theta,q)\phi(\theta,q)=2U_0(\theta,q)^2a(\theta)q\\&=\frac{2a(\theta)q}{z(\theta)[c_0(\theta)+q^2a'(\theta)]} .\end{aligned} \tag{31}$$

It follows that

$$q>0\Longrightarrow U(\theta,q)<U(\theta,-q) , \tag{32}$$

i.e., $|u_-|$ exceeds $|u_+|$ when heat is flowing in the direction of increasing x. Thus, in the present theory, a *small pulse propagating in a body conducting heat will travel more slowly in the direction of heat flow than in the opposite direction.*

The following formulas follow from Eqs. (27):

$$(u_+)(u_-)=U(\theta,q)U(\theta,-q)=U_0(\theta,q)^2 , \tag{33a}$$

$$u_+^{-1}+u_-^{-1}=U(\theta,q)^{-1}-U(\theta,-q)^{-1}=2a(\theta)q . \tag{33b}$$

Consider now a small pulse that is perturbing a steady-state solution (θ,q^0) of the system (15), with the constant q^0 in Eqs. (18) and (19) not zero. Take $x_i=0$, $t_i=0$, and $x_r=l>0$, so that the arrival time t_r is the time required for the pulse to travel from $x=0$ to $x=l$ with velocity $u_+(x)=U(\theta(x),q^0)$. For each pair of temperatures θ_1,θ_2, with $0<\theta_1<\theta_2$, let $\theta^{(\alpha)}$ and $\theta^{(\beta)}$ be the uniquely determined steady-state temperature fields obeying the conditions

$$\theta^{(\alpha)}(0)=\theta_2,\quad \theta^{(\alpha)}(l)=\theta_1 , \tag{34a}$$

$$\theta^{(\beta)}(0)=\theta_1,\quad \theta^{(\beta)}(l)=\theta_2 . \tag{34b}$$

Clearly, $\theta_x^{(\alpha)}<0$, $\theta_x^{(\beta)}>0$,

$$\theta^{(\beta)}(x)=\theta^{(\alpha)}(l-x) , \tag{35}$$

and for the corresponding spatially and temporally constant fluxes of heat, $q^{(\alpha)},q^{(\beta)}$, we have

$$q^{(\alpha)}=-\kappa(\theta^{(\alpha)})\theta_x^{(\alpha)}>0 , \tag{36}$$

$$q^{(\beta)}=-q^{(\alpha)} . \tag{37}$$

If we write $t_r^{(\alpha)}$ for the arrival time at $x=l$ of the pulse when the underlying (unperturbed) temperature field is

$\theta^{(\alpha)}$, and $t_r^{(\beta)}$ when the underlying field is $\theta^{(\beta)}$, then, by Eqs. (28), (29), (35), and (37),

$$t_r^{(\alpha)}=\int_0^l U(\theta^{(\alpha)}(\xi),q^{(\alpha)})^{-1}d\xi \ , \tag{38a}$$

$$\begin{aligned} t_r^{(\beta)}&=\int_0^l U(\theta^{(\beta)}(\xi),q^{(\beta)})^{-1}d\xi \\ &=\int_0^l U(\theta^{(\alpha)}(\xi),-q^{(\alpha)})^{-1}d\xi \ . \end{aligned} \tag{38b}$$

As $q^{(\alpha)}>0$, (32) yields $t_r^{(\alpha)}>t_r^{(\beta)}$. Thus, the time it takes a small pulse to traverse a steady-state temperature field $\theta^{(\alpha)}$ in which the pulse propagates into colder regions exceeds the time the pulse requires to traverse $\theta^{(\beta)}$, the reversal of $\theta^{(\alpha)}$, given by Eq. (35). For the difference of these times, we have, by Eqs. (38), (27), (33), (34), and (36), the remarkably simple formulas,

$$\Delta t=t_r^{(\alpha)}-t_r^{(\beta)}=2q^{(\alpha)}\int_0^l a(\theta^{(\alpha)}(\xi))d\xi \tag{39}$$

and

$$\Delta t=2\int_{\theta_1}^{\theta_2} a(\theta)\kappa(\theta)d\theta \ . \tag{40}$$

If $\Delta\theta=\theta_2-\theta_1$ is small and if the interval (θ_1,θ_2) contains θ_m, the temperature at which κ attains its maximum value, $\kappa_m=\kappa(\theta_m)$, then Eq. (40) yields

$$\Delta t=2\kappa_m\int_{\theta_1}^{\theta_2} a(\theta)d\theta+O((\Delta\theta)^3) \ . \tag{41}$$

More generally,

$$\Delta t=\Gamma(\bar\theta)\Delta\theta+O((\Delta\theta)^2) \ , \tag{42}$$

where

$$\Gamma(\bar\theta)=2\kappa(\bar\theta)a(\bar\theta)>0 \ , \tag{43}$$

and $\bar\theta$ is an arbitrary number between θ_1 and θ_2, such as $(\theta_1+\theta_2)/2$. When $\theta_1<\theta_m<\theta_2$, the difference Δt in transit times is governed by the temperature dependence of the relaxation time for dissipative processes, τ; for, if in Eq. (43) we set $\bar\theta=\theta_m$, Eqs. (10) and (11) yield

$$\Gamma(\theta_m)=\frac{2}{\theta_m}\tau(\theta_m)-\tau'(\theta_m) \ . \tag{44}$$

Of course, the time required for a pulse to traverse a sample of length l in equilibrium with $q\equiv 0$ and θ constant is $t^0=l/\hat U(\theta)$. As $\hat U(\theta)=U(\theta,0)=U_0(\theta,0)$, when $\Delta\theta$ in Eq. (42) is small, Eqs. (38) and (27) yield, for $\bar t=(t_r^{(\alpha)}+t_r^{(\beta)})/2$,

$$\bar t=t^0+O(\Delta\theta)=l/\hat U(\bar\theta)+O(\Delta\theta) \ , \tag{45}$$

where $\bar\theta$ again may be assigned any value in the interval (θ_1,θ_2). In this same limit of small $\Delta\theta$, we have, to a good approximation, at each point, $\theta_x^{(\alpha)}=-\theta_x^{(\beta)}=-\Delta\theta/l$. Equations (42) and (45) yield

$$\frac{\Delta t}{\bar t g}=\Gamma(\bar\theta)\hat U(\bar\theta)+O(g) \ , \tag{46a}$$

or, by Eqs. (10), (11), (21), and (43),

$$\frac{\Delta t}{\bar t g}=-\kappa(\theta)\theta^2[z(\theta)c_0(\theta)]^{-1/2}\frac{d}{d\theta}\left[\frac{z(\theta)}{\theta^2}\right]\Bigg|_{\theta=\bar\theta} +O(g) \ , \tag{46b}$$

where $g=\Delta\theta/l$ is the mean temperature gradient. When θ_m is in (θ_1,θ_2), we can write

$$\begin{aligned}\frac{\Delta t}{\bar t g}&=\Gamma(\theta_m)\hat U(\theta_m)+O(g)\\ &=\hat U(\theta_m)\left[\frac{2\tau(\theta_m)}{\theta_m}-\tau'(\theta_m)\right]+O(g) \ .\end{aligned} \tag{47}$$

To measure Δt and $\Delta t/\bar t=2(t_r^{(\alpha)}-t_r^{(\beta)})/(t_r^{(\alpha)}+t_r^{(\beta)})$, one may, in principle, use a single sample and one steady-state temperature field $\theta^{(\alpha)}$ but measure transit times for pulses moving in opposite directions; $t_r^{(\alpha)}$ is then the transit time to $x=l$ of a pulse originating at $x=0$ when the unperturbed temperature field is $\theta^{(\alpha)}$, and $t_r^{(\beta)}$ the transit time to $x=0$ of a pulse originating at $x=l$ for the same unperturbed field $\theta^{(\alpha)}$.

III. ESTIMATES OF $a(\theta)$ AND $\Gamma(\theta)$

We now seek to calculate the magnitude of the effect described by Eqs. (39), (40), and (46) using published studies of heat pulses propagating into regions in equilibrium with $q=0$ and $\theta=$const.

The propagation of second sound in the ⟨100⟩ direction of NaF was demonstrated by Jackson, Walker, and McNelly[12] shortly after evidence for the phenomenon in NaF was obtained by McNelly *et al.*[38] The NaF crystal studied by Jackson, Walker, and McNelly was of exceptional purity with $\theta_m=16.5$ K, and $\kappa_m=\kappa(\theta_m)=2.4\times 10^9$ ergs sec^{-1}cm^{-1}K^{-1}. In the temperature range $10.0\le\theta\le 18.5$ K, heat pulses were observed with properties expected of second sound. The speed of such a pulse is taken to be the ratio of the observed transit time to the sample length l in the direction of propagation. (Here, $l=0.83$ cm.) It appears appropriate to set the transit time equal to the time of arrival of the pulse peak, which is better defined than the leading edge of the pulse. For our present calculations, we consider each pulse speed so obtained to be a value of $\hat U(\theta)$, where θ is the (equilibrium) temperature of the sample in which the pulse is propagating. We have found that the values of $\hat U$ obtained in this way from the data given in Ref. 12 can be described by a relation of the form,[39]

$$\hat U(\theta)^{-2}=A+B\theta^n \ , \tag{48}$$

where, for θ in K and $\hat U$ in cm sec^{-1},

$$n=3.10,\quad A=9.09\times 10^{-12},\quad B=2.22\times 10^{-15} \ . \tag{49}$$

See Fig. 1. [The reader will note that, in view of Eq. (21), an empirical relation for $\hat U(\theta)$ with the form seen in Eq. (48) gives an algebraically convenient expression for $z(\theta)c_0(\theta)$, namely $A+B\theta^n$; as z' occurs in Eq. (11), this convenience was sought. No deep physical significance should be attributed to the form of Eq. (48).] In the range in which second sound is observed, the values of c_0 calculated for NaF by Hardy and Jaswal[40] are satisfactorily described by

$$c_0(\theta)=\alpha\theta^3 \ , \tag{50}$$

with[41]

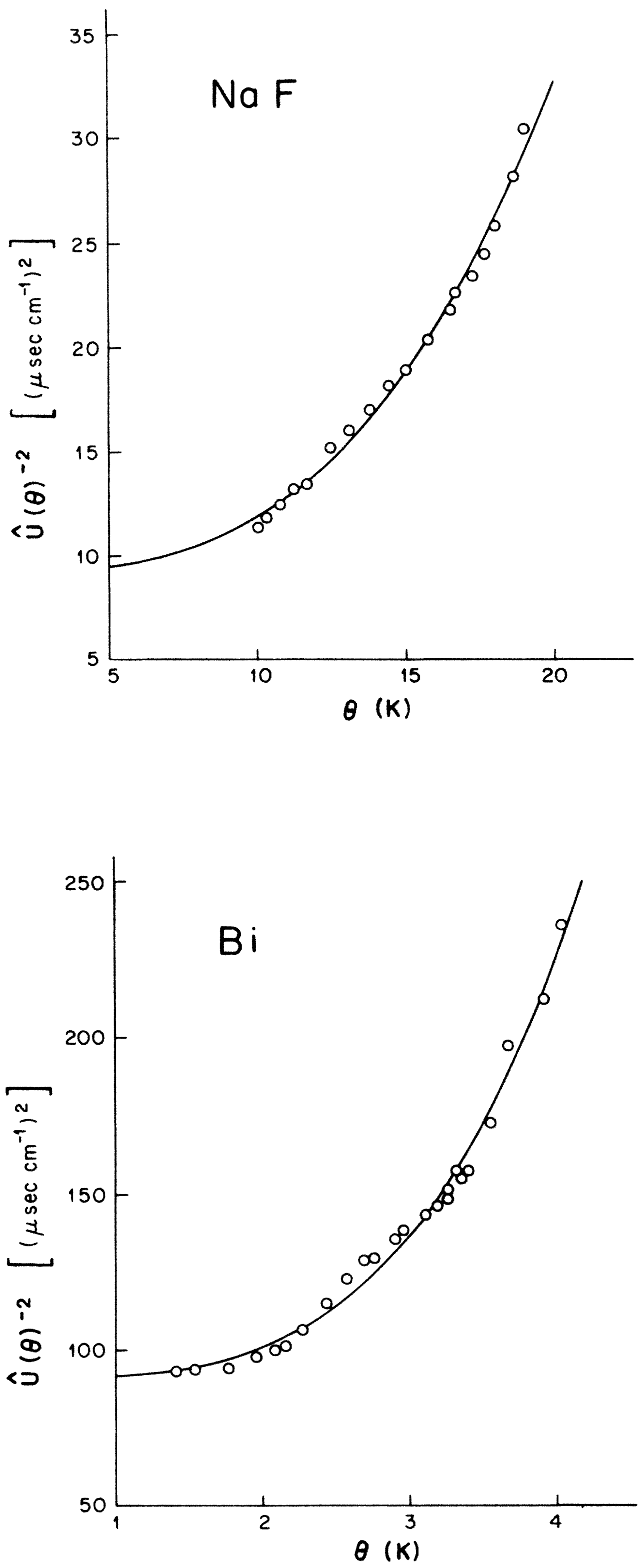

FIG. 1. Comparison of the empirical relation seen in Eq. (48) (——) with observations of transit times for pulses in high-purity crystals in equilibrium at $q=0$. For NaF the data were obtained from Ref. 12, and n, A, B are as in Eqs. (49). For Bi the data are from Ref. 13, and n, A, B are as in Eqs. (53).

$$\alpha = 23 \text{ ergs cm}^{-3}\,\text{K}^{-1} . \tag{51}$$

In a pure Bi crystal, the concentration of free carriers is small at low temperatures and heat transfer is effected by phonons. Kopylov and Mezhov-Deglin[42] reported that for a Bi sample of high purity, $\theta_m = 3.5$ K and $\kappa_m = 3.0\times 10^8$ ergs sec^{-1} cm^{-1} K^{-1}; they remarked that in the range 1.3–6 K, Bi obeys Eq. (50), with

$$\alpha = 550 \text{ ergs cm}^{-3}\,\text{K}^{-1} . \tag{52}$$

Working with Bi crystals of apparently comparable purity, Naryanamurti and Dynes[13] observed second-sound pulses in Bi in the temperature range $1.4 \le \theta \le 4.0$ K. The pulse speed at $\theta = 3.4$ K (which is close to θ_m) was found to be approximately independent of orientation, i.e., was $(7.8\pm 0.5)\times 10^4$ cm sec^{-1} for each of the three mutually orthogonal axes along which propagation occurs. For one case Narayanamurti and Dynes report data from which $\hat{U}$ can be computed as a function of θ. The data are given in a plot of observed arrival times of pulse peaks versus temperature for propagation along the three-fold axis of symmetry of a Bi crystal with $l = 0.386$ cm; we have found that the data can be described by Eq. (48) with[39]

$$n = 3.75, \quad A = 9.07\times 10^{-11}, \quad B = 7.58\times 10^{-13} . \tag{53}$$

(See Fig. 1.)

Equations (48), (50), (21), and (11) yield[25]

$$\alpha z(\theta) = A\theta^{-3} + B\theta^{n-3} , \tag{54}$$

$$\alpha a(\theta) = \tfrac{5}{2} A\theta^{-4} + \frac{5-n}{2} B\theta^{n-4} . \tag{55}$$

As α, A, and B are positive, and the data for NaF and Bi yield $n<4$, the relations (22a) and (22b) both hold here, and the critical value of q in Eqs. (23) and (24) is

$$q_*(\theta) = \alpha\theta^4[10A + \tfrac{1}{2}(5-n)(4-n)B\theta^n]^{-1/2} . \tag{56}$$

Let us now suppose that θ_1 and θ_2 in Eqs. (34) are such that $\theta_1 < \theta_m < \theta_2$. The general formula, Eq. (40), then yields Eq. (41), and if we use Eq. (55) to evaluate $a(\theta)$ in Eq. (41), we have, to within an error $O((\Delta\theta)^3)$,

$$\Delta t = \frac{-\kappa_m}{\alpha} \left[\frac{5A}{3\theta^3} - \frac{5-n}{n-3} B\theta^{n-3} \right]_{\theta_1}^{\theta_2} . \tag{57}$$

Substitution of Eq. (55) into Eq. (43) yields, by Eq. (42), to within $O(\Delta\theta)$,

$$\begin{aligned} \frac{\Delta t}{\Delta\theta} &= \Gamma(\theta_m) = 2\kappa_m a(\theta_m) \\ &= \frac{\kappa_m}{\alpha}[5A\theta_m^{-4} + (5-n)B\theta_m^{n-4}] , \end{aligned} \tag{58}$$

and, by Eq. (47), to within $O(g)$ with $g = \Delta\theta/l$,

$$\frac{\Delta t}{lg} = \Gamma(\theta_m)\hat{U}(\theta_m) = \frac{5A\theta_m^{-4} + (5-n)B\theta_m^{n-4}}{(A + B\theta_m^n)^{1/2}\alpha}\kappa_m . \tag{59}$$

Employing the values of the material parameters θ_m, κ_m, n, A, B, and α given above, we find that, for NaF, $\Gamma(\theta_m)=9.9\times10^{-8}$ sec K^{-1} and $\Gamma(\theta_m)\hat{U}(\theta_m)=0.021$ cm K^{-1}; for Bi, $\Gamma(\theta_m)=2.0\times10^{-6}$ sec K^{-1} and $\Gamma(\theta_m)\hat{U}(\theta_m)=0.15$ cm K^{-1}. Therefore,

$$\Delta t/t_m^0 \cong 0.021\Delta\theta/l \quad \text{for NaF} , \tag{60a}$$

$$\Delta t/t_m^0 \cong 0.15\Delta\theta/l \quad \text{for Bi} . \tag{60b}$$

Here, t_m^0, the transit time through a sample of length l in equilibrium with $q=0$ and $\theta=\theta_m$, differs by $O(\Delta\theta)$ from $\bar{t}$. [For the NaF crystal of Ref. 12, $t_m^0=3.9\times10^{-6}$ sec. For the Bi crystal of Ref. 13, we take θ_m to be 3.5 K which yields 5.1×10^{-6} sec for $t_m^0=l/\hat{U}(\theta_m)$.]

Using Eq. (60a) we find that, for the NaF crystal of Ref. 12, if $\theta_2=17.5$ K and $\theta_1=15.5$ K (so that $\Delta\theta/l=2.4$ K cm^{-1}), $\Delta t/t_m^0$ (i.e., $\Delta t/\bar{t}$) should be $\sim5\%$. [The ratio of the steady-state heat flux to the critical value given by (56), i.e., the ratio $q^{(\alpha)}/q_*$, should then be $\sim3.4\%$.] Equation (60b) implies that, for the Bi crystal of Ref. 13, if $\theta_2=3.562$ K and $\theta_1=3.438$ K (so that $\Delta\theta/l=0.321$ K cm^{-1}), $\Delta t/t_m^0$ should be $\sim5\%$ (and $q^{(\alpha)}/q_*\sim3.5\%$). Thus we find an appreciable value for the ratio $\Delta t/\bar{t}$ under conditions in which the temperature gradient $\Delta\theta/l$ and the steady-state heat flux are large, but not nearly large enough to imply inapplicability of the theory because of failure to meet the condition $|q|<q_*$. As κ_m in Eq. (58) is sensitive to crystal purity, larger values of $\Delta t/\bar{t}$ are expected for the same values of $\Delta\theta/l$ when samples of higher purity are studied. Moreover, for a given material and value of $\Delta\theta$, Δt is approximately independent of l, and hence larger values of Δt can be obtained at smaller values of the temperature gradient, if samples of greater length are used. Because our calculations are based on data for samples of a purity and size known to be realizable, and, in fact, obtained some time ago, they yield conservative estimates for attainable values of Δt and $\Delta t/\bar{t}$.

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[34]A recently developed theory of the regularity of solutions and the stability of equilibrium (Ref. 26) for the full nonlinear system (15) can be invoked to justify the linearization of (15) to (20) for sufficiently small perturbations of equilibrium states.

[35]Some properties of the system (15) for $|q|>q_*$ were discussed by Coleman and Owen (Ref. 25). While their observation that the Eqs. (15) cannot have smooth, periodic, traveling wave solutions is correct, their treatment of periodic traveling waves with discontinuities is speculative and mathematically incomplete. It was recently found (Ref. 26) that the periodic discontinuous fields that they constructed (for $|q|>q_*$) obey only one of the two jump conditions required of distributional solutions of Eqs. (15) when the first of those equations is in the form $q_t+\tau(\theta)^{-1}q+\tau(\theta)^{-1}\kappa(\theta)\theta_x=0$.

[36]The characteristic slopes here equal the possible velocities of a temperature-rate wave, i.e., of a singular surface across which θ and q are continuous but their first derivatives suffer jump discontinuities. Coleman and Owen (Ref. 25) obtained formulas equivalent to the expressions (27) for u_+ and u_- by specializing results obtained by Coleman, Fabrizio, and Owen (Ref. 23) in their study of temperature-rate waves in a three-dimensional context in which the heat flux is not assumed parallel to the direction of motion of the singular surface. [In particular, the formula for ϕ given in Ref. 25 can be cast into the simpler form seen here in Eq. (27c).]

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