

Thermal Conductivity and Anharmonic Forces

M. A. Black

Citation: [American Journal of Physics](#) **41**, 691 (1973); doi: 10.1119/1.1987331

View online: <https://doi.org/10.1119/1.1987331>

View Table of Contents: <http://aapt.scitation.org/toc/ajp/41/5>

Published by the [American Association of Physics Teachers](#)

Articles you may be interested in

[Introduction to Field Operators in Quantum Mechanics](#)

[American Journal of Physics](#) **41**, 678 (1973); 10.1119/1.1987330

[Nanoscale thermal transport. II. 2003–2012](#)

[Applied Physics Reviews](#) **1**, 011305 (2014); 10.1063/1.4832615

[Strain field fluctuation effects on lattice thermal conductivity of ZrNiSn-based thermoelectric compounds](#)

[Applied Physics Letters](#) **85**, 1140 (2004); 10.1063/1.1783022

[Nanoscale thermal transport](#)

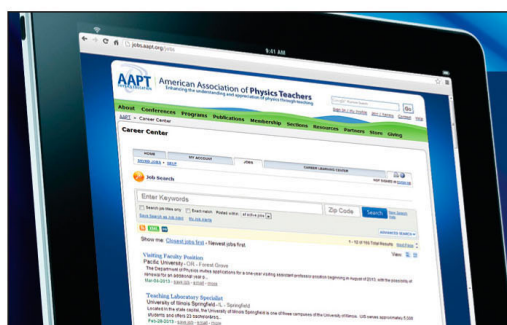
[Journal of Applied Physics](#) **93**, 793 (2003); 10.1063/1.1524305

[Intrinsic lattice thermal conductivity of semiconductors from first principles](#)

[Applied Physics Letters](#) **91**, 231922 (2007); 10.1063/1.2822891

[Some properties of semiconducting IrSb₃](#)

[Journal of Applied Physics](#) **76**, 1665 (1994); 10.1063/1.357750



American Association of **Physics Teachers**

Explore the **AAPT Career Center** –
access **hundreds of physics education and
other STEM teaching jobs** at two-year and
four-year colleges and universities.

<http://jobs.aapt.org>



Thermal Conductivity and Anharmonic Forces

M. A. BLACK

Department of Pure and Applied Physics

University of Salford

Salford, Lancashire

England

(Received 30 April 1971; revised 14 November 1972)

A common model of a solid assumes a regular lattice of atoms which interact via perfectly harmonic forces. Although this model can explain many properties of solids, it is unable to explain why the thermal conductivity of dielectric crystals is not infinite. The source of the problem lies in the slightly anharmonic nature of the forces involved. The following article describes a simple model which allows the effect of the anharmonic forces to be calculated and the thermal conductivity estimated. The results are in agreement with other methods of calculation.

The transport of heat through a solid takes place either via the conduction electrons, the lattice vibrations, or possibly both. In an insulator the dominant conduction mechanism is the lattice vibrations. Heat enters the specimen at one end, the rise in temperature causes the atoms to vibrate more vigorously, and this vibration (energy) is passed down the crystal via the forces which link the atoms together. For many purposes it is sufficient to regard these forces as harmonic in character. Such an approach is adequate in a simple treatment of specific heat, for example, where one can regard the solid as consisting of a regular lattice of point masses, each executing simple harmonic motion.

The problem is more complicated than this of course, because each atom vibrates in a random direction which is itself continuously changing. To avoid the difficulties of such a many-body problem one analyzes the vibrations of all the atoms in

the crystal in terms of a spectrum of travelling waves which together give rise to the same final atomic motions. These waves are then grouped into packets, or quantized, and are called phonons (by analogy with photons in light). It is then convenient to regard the crystal as a "box of phonons" so that a change in temperature corresponds to a change in the phonon distribution with frequency, and a transport of heat corresponds to phonons travelling through the "box." Although this approach can be used in the treatment of specific heat (as in Debye theory), it turns out to be completely inadequate for thermal conductivity and predicts an infinite conductivity.

To produce a finite conductivity it is necessary to allow for the fact that the interatomic forces are not perfectly harmonic. In other words, the potential energy as a function of interatomic separation for the crystal is given by an expression such as

$$V = ax^2 + bx^3 + cx^4 + \dots, \quad (1)$$

where V is the potential energy; x is the displacement of atoms from equilibrium, and a, b, c, \dots are constants. The harmonic approximation corresponds to all coefficients except " a " being zero.

If we ask how a finite thermal conductivity arises we see that it requires that the phonons which carry the heat through the crystal be scattered every so often so as to interrupt their steady flow. In other words, we require that the phonons have a noninfinite mean free path. A similar situation occurs, for example, in electrical conduction in metals and in mass flow (viscosity) in gases. (See, for example, Tabor.¹) In calculating thermal conductivity, K , we are interested in a flow of heat so that the parameters of interest are the thermal capacity of the carriers (i.e. the phonons) and their velocity. By following an analogous argument to the one used in the case of viscosity in gases it may be shown^{1,2} that the thermal conductivity is given by

$$K = \frac{1}{3} C v l, \quad (2)$$

where C is thermal capacity of carriers (phonons),

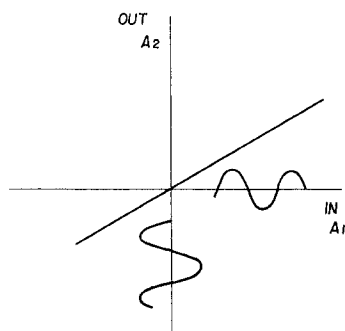


Fig. 1. Linear response.

u is velocity of carriers, l is mean free path. It is here that our problem arises. If one considers the interaction of phonons in a perfectly harmonic system, one finds that no scatter occurs, i.e., the flow of energy is not interrupted and the mean free path (and K with it) is infinite. Only when the interaction is anharmonic is some energy removed from the incident phonons and transferred to other frequencies, which we may interpret as scattering. This may be appreciated by considering a familiar example from another field. Imagine a plane wave incident on the ear, or perhaps a sinusoidal input to a vacuum tube or transistor circuit. If the response of the ear or other device is linear, one will obtain an output consisting of the input frequency only (see Fig. 1), or if $A_2 = \alpha A_1$, and $A_1 = a_1 \cos \omega t$, then $A_2 = \alpha a_1 \cos \omega t$.

If the device is nonlinear, then new frequencies will appear in the output (see Fig. 2). In this case the bottom half of the output waveform is flattened so that harmonics have appeared. It is easy to see that this distortion corresponds in a simple case to the presence of second harmonic and it is also easy to calculate the amplitude of this second harmonic in terms of the response curve of the system. One way is to let $A_2 = \alpha A_1 + \beta A_1^2$, so that A_2 becomes $\alpha a_1 \cos \omega t + \beta a_1^2 \cos^2 \omega t$ and $\cos^2 \omega t$ may be expressed in terms of $\cos 2\omega t$.

If we look at what we have just done, we see at once the connection with phonons travelling through a solid. Thus we imagine the phonons being absorbed by the first atom and causing it to oscillate, thus re-emitting phonons which pass on to the next atom and so on down the chain. Each absorption, however, is really an anharmonic process so that at each atom some fraction of the incident phonon is "lost" to other frequencies.

Our approach then will be to determine this "fraction" which is transferred into other frequencies and hence to derive an expression for the mean free path.

Before we do this, we should appreciate the limitations of our approach. We have suggested that phonon interaction can only occur if we include an anharmonic term in the interaction forces. Since, however, the phonons are themselves really just vibrations of the lattice, we should really talk of phonon-phonon interactions. If we do this we find that such collisions *conserve momentum* so that we are still unable to provide a mechanism for finite thermal conductivity. It was in order to overcome this dilemma that Peierls postulated the concept of an Umklapp process¹ in which the phonon suffers a Bragg reflection. However, our present treatment is still important in that it shows us how phonons are able to interact, and such normal processes (as distinct from Umklapp processes) do play a part in determining the phonon distribution as a function of temperature.

For simplicity we will let the lattice potential energy be

$$V = ax^2 + bx^3, \quad (3)$$

(which we can relate to $A_2 = \alpha A_1 + \beta A_1^2$; see below).

Plotting this equation, and taking b as negative, gives us the familiar curve shown in Fig. 3(b) which should be compared with the harmonic potential well obtained by setting $b = 0$ in Eq. (3). [See Fig. 3(a).]

To obtain the force acting on an atom when it is displaced from equilibrium we take $-dV/dx$, giving us $(-2ax - 3bx^2)$ which is shown graphically in Fig. 4. This graph shows also the harmonic curve, which is simply Hooke's law. If we use this

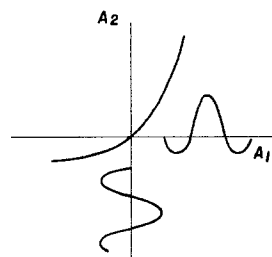


Fig. 2. Anharmonic response.

graph to illustrate the response of an atom to an incoming phonon, we may calculate the relative amplitudes of the fundamental and second harmonic as shown in Fig. 5.

The explicit effect of second harmonic is seen in the graph given in Fig. 6. It is also possible to treat the interaction of two incoming phonons of different frequency in a similar manner. If two phonons interact in a harmonic system they add by superposition giving rise to beats (see Fig. 7). If this takes place in an anharmonic system, however, the beats' envelope is distorted (as for a single wave) and one has the result shown in Fig. 8. Looking at this graph we see how the beat or difference frequency is emphasized by the non-linearity of the system.

To summarize, then, we have shown that if one has two incoming phonons of frequencies ω_1 and ω_2 interacting with an atom which is held by

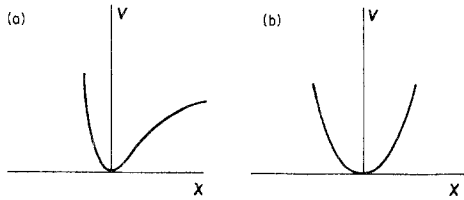


FIG. 3. (a) Harmonic potential well. (b) Anharmonic potential well.

anharmonic forces, then one will expect to generate not only phonons of frequency ω_1 and ω_2 but also of $2\omega_1$, $2\omega_2$, and $\omega_1 - \omega_2$ at least, (as well as $\omega_1 + \omega_2$). We have also suggested that the fractional amplitude of phonons in the fundamental frequencies as compared with the harmonics is given by a term of the form

$$2ax/3bx^2 = 2a/3bx = f_1. \quad (4)$$

We should notice that although we have adopted a graphical approach to this problem, we could have attacked it mathematically. Thus, we let

$$V = ax^2 + bx^3$$

so that

$$dV/dx = 2ax + 3bx^2.$$

The response of the system to an input con-

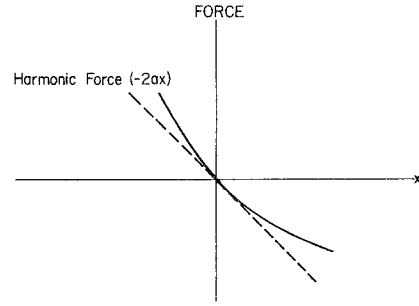


FIG. 4. Force (anharmonic system).

sisting of two driving forces $F \cos \omega_1 t$ and $F \cos \omega_2 t$ will then be given by the solution of the equation

$$\ddot{x} + 2ax + 3bx^2 = F(\cos \omega_1 t + \cos \omega_2 t). \quad (5)$$

In the approximation that $2ax \gg 3bx^2$ this equation is shown in the Appendix to have a solution of the form $x = x_0 + \Delta$, where x_0 is the solution of Eq. (5) when b is zero, namely,

$$x_0 = (F/2a)(\cos \omega_1 t + \cos \omega_2 t), \quad (6)$$

and

$$\Delta = (3bF^2/16a^3)[\cos 2\omega_1 t + \cos 2\omega_2 t + 2 \cos(\omega_1 + \omega_2)t + 2 \cos(\omega_1 - \omega_2)t + 2]. \quad (7)$$

In order to compare this with the result of our graphical approach, we really require the ratio x_0/Δ , which should then be compared with the value $2a/3bx$, (Eq. 4). Both x_0 and Δ contain terms of the form $\cos \omega t$, but a simple way of considering that ratio x_0/Δ is to omit the cosine factors and take the amplitudes so that the ratio

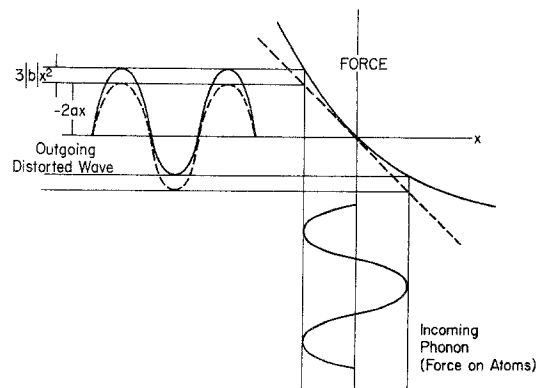


FIG. 5. Anharmonic response giving distortion.

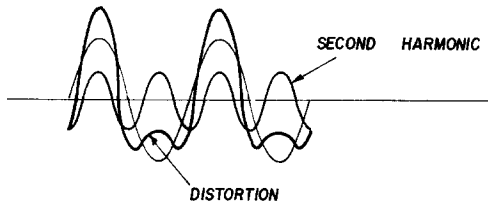


FIG. 6. Superposition of waves.

x_0/Δ may be written as

$$x_0/\Delta = (F/a) \cdot (16a^3/24bF^2) = 2a^2/3bF.$$

(This solution is dealt with more fully in the Appendix.) Furthermore, since $F = -2ax$ in the harmonic approximation, it follows that

$$x_0/\Delta = a/3bx, \quad (8)$$

which is similar to our graphical solution, where we obtained a ratio of $2a/3bx$ (Eq. 4).

The expression $(a/3bx)$ is a measure of the fraction of fundamental mode that "survives" each interaction. We are really interested in the fraction of the *energy* that is lost from the fundamental mode in each collision rather than the amplitude. Since the energy is proportional to the square of the amplitude we can see that the fraction, f_2 , of the energy lost from the fundamental mode is dependent on a term

$$f_2 = 9b^2x^2/a^2 = (\Delta/x_0)^2. \quad (9)$$

In such a process, where a given *fraction* of the energy is lost in each collision, one cannot ask how many collisions are necessary in order to remove *all* the energy from the fundamental mode. Instead, we will try and estimate the fraction f_2 , given by Eq. (9), and then go on to calculate how many collisions are necessary to reduce the original energy by some reasonable factor. Thus, suppose we assume an anharmonic contribution to the lattice potential energy of

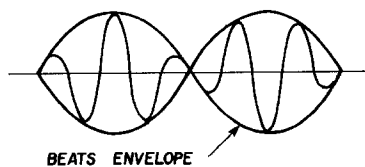


FIG. 7. Beats (harmonic).

about 10%, Eq. (3). We then have

$$bx^3 = 0.1ax^2. \quad (10)$$

Substituting this into Eq. (9) yields a value for f_2 of 9×10^{-2} or 9 percent. In other words each collision (or interaction) reduces the energy in the fundamental mode by 9%. In general, after n such collisions the energy will be reduced to a fraction $(0.91)^n$ of its original value. Substituting for n into this expression tells us that after twenty collisions the energy remaining is 15% of the original; after fifty collisions it is approximately 1%. In order to obtain an estimate of the mean free path let us take $n = 50$ so that almost all the original energy has been dissipated. If we now assume one collision every lattice spacing r_0 we obtain a mean free path l of $50r_0$.

This value for l is not unreasonable when we

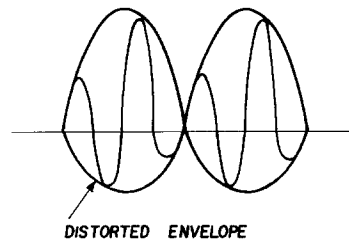


FIG. 8. Beats (anharmonic).

realize how sensitive this is to our guess at the anharmonic content of the lattice energy.

The actual expression for the mean free path will really depend on the criterion we set in deciding how small the fundamental mode is to become for us to be able to ignore it. However, as a guide to orders of magnitude, and certainly for the physical dependencies, the above expression is a useful one. In essence we have now achieved our object; but it is interesting to express the mean free path in a more familiar form so as to bring out the physical dependence more strongly.

It is well known that for a perfectly harmonic lattice the thermal expansion coefficient is zero (if we ignore the effects of internal energy), and that in order to arrive at a mechanism for expansion we must allow for the anharmonic contribution to the interatomic forces. A simple one-dimensional approach using our earlier graph of potential (V) versus displacement from

equilibrium (x) together with Eq. (3) yields a thermal expansion coefficient of

$$\alpha = bk/2a^2r_0$$

where k is Boltzmann's constant.^{1,4} Another parameter of importance in the theory of solids is the Gruneisen parameter γ . This may be regarded as a constant relating the specific heat and thermal expansion to other properties of solids³ or (more fundamentally) as a parameter which measures the anharmonic content of the lattice forces directly. A simple one-dimensional approach such as the one adopted in our treatment yields

$$\gamma = 3br_0/4a$$

(Ref. 4). In comparing the expressions for α and γ with those given in standard textbooks it should be remembered that the expressions usually quoted are for a three-dimensional solid whereas our expressions are calculated for a simple one-dimensional case. This leads to the numerical constants being slightly different but the essential physical dependencies remain the same. If we now substitute these expressions for α and γ into the expression for f_2 we obtain

$$f_2 = 9b^2x^2/a^2 = 24ax^2\alpha\gamma/k. \quad (11)$$

However, since $V \simeq ax^2 \simeq kT$, we may write

$$f_2 = 24ax^2\alpha\gamma/k = 24\alpha\gamma T. \quad (12)$$

Returning to Eq. (9) we see that after n collisions the fraction of energy *remaining* in the fundamental mode is simply $(1-f_2)^n$. If we demand that only 1% of the fundamental mode remains we may write

$$(1-f_2)^n = 10^{-2}. \quad (13)$$

Taking logarithms and substituting from Eq. (12) we obtain

$$n \log_e(1-24\alpha\gamma T) = -4.6. \quad (14)$$

Remembering that $f_2 \ll 1$ and expanding the logarithm to first order only yields $n = 4.6/24\alpha\gamma T$

so that finally we obtain

$$l = nr_0 = r_0/5\alpha\gamma T. \quad (15)$$

Equation (15) is very interesting. It shows us how the mean free path, and hence the conductivity, depends on the anharmonic forces between atoms and how a simple T^{-1} dependence arises. We should not, of course, place any reliance on the numerical factor, which can be made to vary by altering our simple model. The general form of Eq. (7), however, is well known; if numerical values are substituted into it, one obtains good agreement with experiment.⁵

APPENDIX

For simplicity we will let

$$V = ax^2 + bx^3, \quad (A-1)$$

and we will consider a single atom or oscillator being excited by two phonons which we will regard as having frequencies ω_1 and ω_2 . It follows from Eq. (A-1) that the response of the atom to the incident phonons is given by the equation

$$\ddot{x} + Ax + Bx^2 = F \cos\omega_1 t + F \cos\omega_2 t, \quad (A-2)$$

where x is displacement from equilibrium. $F \cos\omega_1 t$ and $F \cos\omega_2 t$ represent the displacing forces due to the incident phonons (and we have let F be the same for both for simplicity) and A and B follow from taking $(-dV/dx)$ in Eq. (A-1) and are $2a$ and $3b$, respectively.

We will now solve Eq. (A-2) for x and determine the amplitude of the terms in ω_1 and ω_2 and also those in other frequencies (which we expect to contain harmonics of ω_1 and ω_2 and also sum and difference frequencies). This will enable us to decide how much of the incident energy has been scattered and lead us to an estimate of the mean free path for the phonons.

If $B=0$ in Eq. (A-2), we have the familiar solution

$$\begin{aligned} x &= [F \cos\omega_1 t / (A - \omega_1^2)] + [F \cos\omega_2 t / (A - \omega_2^2)] \\ &= X_1 + X_2, \end{aligned} \quad (A-3)$$

where A is usually written as ω_0^2 , and ω_0 is the resonant frequency. Guided by this solution and

supposing the anharmonic term in Eq. (A-1) to be small, we let $x = X_1 + X_2 + \Delta$, where Δ is small (hopefully). Thus

$$\ddot{x} = -(X_1\omega_1^2 - X_2\omega_2^2) + \ddot{\Delta}. \quad (\text{A-4})$$

Substituting into Eq. (A-2) we obtain

$$\begin{aligned} & -(X_1\omega_1^2 + X_2\omega_2^2) + \ddot{\Delta} \\ & + A(X_1 + X_2 + \Delta) + B(X_1 + X_2 + \Delta)^2 \\ & = F \cos\omega_1 t + F \cos\omega_2 t. \end{aligned} \quad (\text{A-5})$$

We now use Eq. (A-3) together with the principle of superposition, which allows us to separate the terms in ω_1 and ω_2 , giving us

$$\begin{aligned} & F \cos\omega_1 t + F \cos\omega_2 t \\ & = (A - \omega_1^2)X_1 + (A - \omega_2^2)X_2. \end{aligned} \quad (\text{A-6})$$

Subtracting this from Eq. (A-5) yields

$$\ddot{\Delta} + A\Delta + B(X_1 + X_2 + \Delta)^2 = 0, \quad (\text{A-7})$$

or if the anharmonicity is small so that Δ is small,

$$\ddot{\Delta} + A\Delta + B(X_1 + X_2)^2 = 0, \quad (\text{A-8})$$

or

$$\ddot{\Delta} + A\Delta = -B(X_1 + X_2)^2, \quad (\text{A-9})$$

so that we have reduced our problem to the solution of a harmonic oscillator equation in Δ . If we write out X_1 and X_2 in full, Eq. (A-9) becomes

$$\begin{aligned} \ddot{\Delta} + A\Delta = & -BF^2 \left(\frac{\cos^2\omega_1 t}{(A - \omega_1^2)^2} \right. \\ & \left. + \frac{2 \cos\omega_1 t \cos\omega_2 t}{(A - \omega_1^2)(A - \omega_2^2)} + \frac{\cos^2\omega_2 t}{(A - \omega_2^2)^2} \right). \end{aligned} \quad (\text{A-10})$$

In order to simplify the solution of this equation we let $A \gg \omega_1^2, \omega_2^2$. Since $A = \omega_0^2$ this implies that we consider phonons of frequency much less than

the resonant frequency of the atom. We also use the fact that

$$\cos^2\omega t = \frac{1}{2}(\cos 2\omega t + 1), \quad (\text{A-11})$$

$$\begin{aligned} 2 \cos\omega_1 t \cos\omega_2 t &= \cos(\omega_1 + \omega_2)t \\ &+ \cos(\omega_1 - \omega_2)t, \end{aligned} \quad (\text{A-12})$$

and substitute these into Eq. (A-10), giving

$$\begin{aligned} \ddot{\Delta} + A\Delta = & -(BF^2/A^2) \left[\frac{1}{2} \cos 2\omega_1 t + \frac{1}{2} \cos 2\omega_2 t \right. \\ & \left. + \cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t + 1 \right]. \end{aligned} \quad (\text{A-13})$$

Now the solution to Eq. (A-2) with $B=0$ and $A \gg \omega_1, \omega_2$ is by Eq. (A-3),

$$x = F[(\cos\omega_1 t/A) + (\cos\omega_2 t/A)]. \quad (\text{A-14})$$

It can be seen that Eq. (A-2) (with $B=0$) and Eq. (A-13) have essentially the same form so that the solution to Eq. (A-13) is simply

$$\begin{aligned} \Delta = & \frac{BF^2}{A^2} \left(\frac{\cos 2\omega_1 t}{2A} + \frac{\cos 2\omega_2 t}{2A} + \frac{\cos(\omega_1 + \omega_2)t}{A} \right. \\ & \left. + \frac{\cos(\omega_1 - \omega_2)t}{A} + A^{-1} \right). \end{aligned} \quad (\text{A-15})$$

Finally in order to compare the amplitudes of x and Δ we omit the cosine factors in Eqs. (A-14) and (A-15) leaving us with $x = 2F/A$ and $\Delta = 4BF^2/A^3$. Using the fact that A and B are equal to $2a$ and $3b$, respectively, we have

$$x/\Delta = A^2/2BF = 2a^2/3bF. \quad (\text{A-16})$$

¹ D. Tabor, *Gases, Liquids and Solids*, Penguin Library of Physical Sciences (Penguin, Harmondsworth, England, 1969).

² C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1968).

³ J. K. Roberts and A. R. Miller, *Heat and Thermodynamics* (Blackie, London, 1960), 5th ed.

⁴ M. A. Black, *Phys. Ed.* **7**, 515 (November 1972).

⁵ J. S. Dugdale and D. K. C. MacDonald, *Phys. Rev.* **98**, 1751 (1955).