upon the conductivity mechanism, they do suggest that the number of electrons involved in the conductivity of Fe_3O_4 is large. While the possibility that the observed value of R_0 is small because of partial compensation by positive carriers is not to be ignored, nevertheless the low conductivity of Fe_3O_4 with respect to metals is probably due to a low mobility. The limited data reported here and the low conductivity of $NiOFe_2O_3$ also suggest that the condition of equivalent ions with different valence in identical sites is a necessary condition for conductivity in these materials.

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Thermal Resistance due to Isotopes at High Temperatures

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In pure dielectric crystals, the isotopic variations of atomic mass contribute a temperature-independent thermal resistance at high temperatures. This resistance has been calculated using a Debye model of the vibrational spectrum. Umklapp processes are treated as the dominant scattering mechanism. The distribution of the heat current over the vibrational modes is known for low frequencies. This distribution is considered to apply over the whole frequency spectrum. The calculated result is compared with the experiments of Geballe and Hull on isotopically pure germanium. A satisfactory agreement with experiment is obtained.

In many dielectric crystals heat is transported principally by lattice vibrations. A thermal resistance, or finite thermal conductivity, results from interactions between phonons and from the scattering of phonons by crystal imperfections. In pure crystals of a single chemical constituent, with which this paper is concerned, the natural isotopic variations of atomic mass will scatter phonons. In contrast to phonon-phonon scattering which increases with temperature, the scattering of phonons by mass variations is temperature independent. Thus, at high temperatures isotopic scattering does not affect the steady-state distribution of phonons in a temperature gradient and simply leads to an additional resistance independent of the temperature.[1] It is the aim of this paper to calculate that resistance.

The scattering of phonons by mass irregularities is calculable from first principles. Klemens[2] has shown that it is described by a relaxation time, τ_I, which in the Debye approximation is given by

$$1/\tau_I(\omega)=\Omega\Gamma\omega^4/4\pi c^3\equiv A\omega^4,$$

where (1)

$$\Gamma=\textstyle\sum_i f_i(\Delta m_i/m)^2.$$

Here Ω is the volume per atom of the crystal, f_i is the fraction of atoms with mass variation Δm_i, m is the average mass of all atoms, c is the velocity of sound in the Debye model, and ω is the phonon frequency. We see that isotopes are most effective in scattering short-wavelength phonons. Even in this region, though, the temperature independence of isotope scattering will result in its being a small effect at high enough temperatures.

Umklapp processes are the dominant scattering mechanism at high temperatures. Umklapp scattering for low-frequency phonons has been treated by Klemens,[3] who has shown that at low temperatures it is describable to first order by a relaxation time, τ_U, such that

$$\tau_U\propto 1/\omega^2,\quad \omega\ll\omega_D, \tag{2}$$

where ω_D is the Debye limiting frequency. The expression (2) can be shown to be also valid at high temperatures.

We shall consider that all long-wave phonons are scattered in the same way. In general, special consideration must be given to the long-wave longitudinal phonons, for it is well known that such phonons cannot take part in Umklapp processes. However, Herring[4] has shown that in crystals of high enough symmetry long-wave longitudinal phonons are converted into transverse phonons, by ordinary momentum conserving 3-phonon processes, rapidly enough to avoid a low-frequency catastrophe in the conductivity. In particular, for cubic materials the relaxation time for this process

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[1] This point is discussed by R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1955), p. 52.

[2] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

[3] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

[4] C. Herring, Phys. Rev. **95**, 954 (1954).

is inversely proportional to the square of the phonon frequency.

For phonons of higher frequency, it is not possible to deduce the frequency dependence of Umklapp scattering from simple arguments. However, we shall make the assumption that the dominant scattering may be described by the expression (2) over the entire frequency range.

The expression for the heat conductivity, κ, when the scattering is describable by a relaxation time is[2]

$$\kappa=\frac{1}{3V}\sum_k C(k)v^2(k)\tau(k). \tag{3}$$

Here V is the volume of the crystal; k denotes the wave vector and the polarization of a vibrational mode; C is the specific heat due to the mode k, (at temperatures greater than the Debye temperature, this specific heat is equal to K, the Boltzmann constant); v is the phonon group velocity; and τ is the relaxation time. At high temperatures and in the Debye approximation, Eq. (3) becomes

$$\kappa=\frac{K}{2\pi^2 c}\int_0^{K\theta/\hbar}\omega^2\tau(\omega)d\omega, \tag{4}$$

where θ is the Debye temperature and $\hbar$ is Planck's constant. If we add the scattering rates due to isotopes and Umklapp processes, the combined relaxation time, $\tau(\omega)$, is given by

$$1/\tau(\omega)=(1/\tau_U)+A\omega^4. \tag{5}$$

Since $A\omega^4\tau\ll 1$ for all ω, to good approximation

$$\kappa=\frac{K}{2\pi^2 c}\int_0^{K\theta/\hbar}\omega^2\tau_U d\omega \times\left[1-A\int_0^{K\theta/\hbar}\omega^6\tau_U{}^2 d\omega\bigg/\int_0^{K\theta/\hbar}\omega^2\tau_U d\omega\right]. \tag{6}$$

The resistivity, W, is the inverse of κ. It follows at once from Eq. (6) that the resistance due to isotopes is

$$W_I=\frac{2\pi^2 cA}{K}\int_0^{K\theta/\hbar}\omega^6\tau_U{}^2 d\omega\bigg/\left[\int_0^{K\theta/\hbar}\omega^2\tau_U d\omega\right]^2. \tag{7}$$

Any temperature dependence of the dominant scattering cancels out of this expression. Substituting for A and τ_U from (1) and (2), we get the simple and interesting result

$$W_I=\frac{\pi}{6}\frac{\Omega\Gamma}{c^2}\left(\frac{\theta}{\hbar}\right). \tag{8}$$

DISCUSSION

The result (8) may be compared with a recent experiment. Geballe and Hull[5] have measured the thermal conductivity of an almost isotopically pure crystal of germanium. They report that the difference between the resistance of this crystal and that of ordinary chemically pure germanium tends to the value 0.15 cm °K/watt as the temperature increases. At 400°K this difference is already only 10% of the total resistance.

Slack[6] has calculated Γ for the natural isotopic mixture of germanium; the value he gives is $\Gamma=5.72\times10^{-4}$. For germanium $\Omega=22.6\times10^{-24}$ cm^3, and $\theta=375$°K. The velocity of sound in the Debye approximation is given by $c=(K\theta/\hbar)(\Omega/6\pi^2)^{\frac{1}{3}}$. Calculation yields $c=3.58\times10^5$ cm/sec. Substituting these values into (8), we get a result of 0.19 cm °K/watt. Considering the crudeness of the Debye model used, this is as good an agreement as one might reasonably expect. This agreement indicates that the assumption for the distribution of energy over the vibrational modes is essentially correct. If τ_U were inversely proportional to the frequency, for example, the numerical constant in (8) would be changed to $2\pi/5$ and the calculated resistance to 0.46 cm °K/watt. Even for the crude model used, the disagreement in that case would probably be significant.

The model used in this paper is similar to that used by Callaway[7] in quantitatively explaining the difference between the low-temperature conductivity of natural and isotopically pure germanium. This model is thus adequate for an understanding of the isotopic contribution to the resistance over the whole temperature range.

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[5] T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

[6] G. A. Slack, Phys. Rev. **105**, 829 (1957).

[7] J. Callaway, Phys. Rev. **113**, 1046 (1959).