PHYSICAL REVIEW VOLUME 133, NUMBER 3A 3 FEBRUARY 1964

Phonon Relaxation in Hydrated Crystals*

D. L. MILLS†
Department of Physics, University of California, Berkeley, California
(Received 19 August 1963)

It is shown that a porous layer on the surface of a crystal immersed in liquid helium can result in a surface which is essentially nonreflecting for phonons coming from the interior of the crystal. Such a porous layer may be formed by partial dehydration of the surface of the crystal. This result may explain the phonon relaxation time observed in lanthanum double nitrate by Jeffries, Scott, Benoit, and Ruby.

I. INTRODUCTION

THE values of the phonon relaxation time in lanthanum double-nitrate crystals [$La_2Mg_3(NO)_{12}\cdot 24H_2O$] were inferred by Jeffries, Scott, Benoit, and Ruby[1,2] by studying the spin resonance of rare-earth impurity ions. The measurements were performed at temperatures below 1.5°K. For crystals doped with Pr, Sm, and Ce, frequencies in the range of 9–10kMc/sec were employed, and a frequency of 34.3 kMc/sec was employed for crystals doped with Nd. In all cases the relaxation time, denoted as T_{ph}, was found to lie in the range of 0.11–0.63 μsec. This is roughly the time required for a phonon to travel a distance equal to one-half of the crystal thickness. Jeffries *et al.* defined a mean-free path $\bar{l}=c_sT_{\mathrm{ph}}$, where c_s is the velocity of sound in the crystal, taken to be 2.5×10^5 cm/sec. The mean-free path $\bar{l}$ was then compared to the thickness l of the crystal. The ratio $\bar{l}/l$ was found to lie in the range 0.29–0.82.

A phonon mean-free path of this length suggests that a surface phonemenon may be responsible for limiting the mean-free path. If we consider the reflection of sound from a sharp crystal-liquid helium boundary, it is easy to see that the acoustical impedance mismatch is so great that a phonon mean-free path of many crystal thicknesses would be expected if intrinsic relaxation processes are negligible. The characteristic acoustical impedance Z of a medium is the product of the density and the velocity of sound. The ratio of the characteristic impedance of liquid helium to that of the crystal is

$$\frac{Z_{\mathrm{He}}}{Z_{\mathrm{cr}}}=\frac{\rho_{\mathrm{He}}c_{\mathrm{He}}}{\rho_{\mathrm{cr}}c_{\mathrm{cr}}}=\frac{(0.125)(2.4\times10^4)}{(2)(2.5\times10^5)}\cong\frac{1}{160},$$

where we have employed the values $\rho_{\mathrm{He}}=0.125$ g/cm^3, $c_{\mathrm{He}}=2.4\times10^4$ cm/sec, $\rho_{\mathrm{cr}}=2$ g/cm^3, and $c_{\mathrm{cr}}=2.5\times10^5$ cm/sec. At normal incidence the ratio of the amplitude of the reflected wave to that of the incident wave is

$$R=(Z_{\mathrm{cr}}-Z_{\mathrm{He}})/(Z_{\mathrm{cr}}+Z_{\mathrm{He}})\cong79/80. \qquad (1)$$

Thus, a mean-free path much longer than that observed would be expected. Measurements of the energy reflected from a quartz-liquid helium boundary have been made[3] in which the measured reflection coefficient agrees with that given by Eq. (1).

It is shown below that a thin porous surface layer in which the pores become filled with liquid helium can cause the crystal surface to become almost totally nonreflecting. Viscous effects within such a porous layer can cause the transmitted energy to be dissipated in 10^{-3}–10^{-2} cm. A porous layer of this type might be formed by partial dehydration of the crystal.[4] Porous structures resulting from the dehydration process have been observed in gypsum.[5]

In Sec. II the acoustic properties of a porous structure are discussed from a physical point of view. Estimates are made of the penetration depth of both longitudinal and shear waves in the porous medium. In Sec. III a set of phenomenological equations describing propagation of longitudinal waves in a porous structure with fluid-filled pores is presented. The nature of the solutions to these equations is discussed and a calculation of the reflection coefficient for normally incident sound is given for a wide range of the relevant parameters.

II.

The penetration depth δ of a sound wave propagating in a porous structure may be estimated by a simple calculation. We consider a sound wave propagating in a medium which consists of parallel pores of radius r. We assume the wave vector is parallel to the pores. Let the pores be filled with a fluid characterized by a viscosity coefficient η. The quality factor Q of the system is defined by

$$Q=\text{Energy stored}/(1/\omega)\times\text{Energy dissipated/Unit time}.$$

Consider a slab of unit area and of thickness dx oriented perpendicular to the wave vector. The average kinetic energy of the slab is $\frac{1}{2}\rho\langle v^2\rangle_{\mathrm{av}}dx$ where ρ is the

* Supported by the National Science Foundation.
† National Science Foundation Predoctoral Fellow.
[1] P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 32 (1962).
[2] R. H. Ruby, H. Benoit, and C. D. Jeffries, Phys. Rev. 127, 51 (1962).
[3] B. E. Keen, P. W. Matthews, and J. Wilks, Phys. Letters 5, 5 (1963).
[4] The experiments performed on crystals doped with Ce impurities employed an evacuated cavity. However, it is probable that some helium remained in the cavity after the evacuating procedure. An adsorbed film could then form on the crystal surface and the pores would fill with fluid.
[5] C. Sella and M. F. Sella, *Fifth International Congress for Electron Microscopy* (Academic Press Inc., New York, 1962), Vol. 2, p. 1-9.

mass/unit volume and where $\langle v^2\rangle_{av}$ is the space and time average of the square of the velocity. In the harmonic approximation, the space and time average of the potential energy is equal to that of the kinetic energy so that the total energy stored in the slab is $\rho\langle v^2\rangle_{av}dx$. In general the pressure P will be a function of the three coordinates x, y, and z as well as the time. Here y and z are the coordinates in the plane perpendicular to the wave vector.

Let $P(x,t)$ represent the pressure averaged over y and z. The force driving the slab is $[\partial P(x.t)/\partial x]dx$. The average value of the energy dissipated per unit time is $v\langle\partial P/\partial x\rangle_{av}dx$. If we assume a sinusoidal time dependence, the pressure gradient $\partial p/\partial x$ may be related to the velocity by an equation of the form

$$\partial P/\partial x=-\sigma v\,,$$

where σ is in general a frequency-dependent complex number. The imaginary part of σ is the inertial term and the real part is the dissipative term. Then $\langle\partial P/\partial x\rangle_{av}=-\mathrm{Re}[\sigma]\langle v^2\rangle_{av}$, and we find

$$Q=\omega\rho/\mathrm{Re}[\sigma].$$

We consider now the propagation of a longitudinal wave through the structure. To obtain an expression for $\mathrm{Re}[\sigma]$, consider first a single cylindrical pore of radius r filled with fluid. In the limit of high frequency only that portion of the fluid in the immediate vicinity of the wall is affected by the motion. In this limit, it may be shown that[6]

$$\mathrm{Re}[\sigma]=(2\eta\omega\rho_2)^{1/2}/r\,,$$

where ρ_2 is the density of the fluid. The width Δ of the layer affected by the motion is given[7] by $\Delta=(\eta/\omega\rho_2)^{1/2}$. The above expression is valid if $r/\Delta=(\omega\rho_2r^2/\eta)^{1/2}\gg1$. If $(r/\Delta)<1$, the fluid throughout the pore is affected by the motion and the flow is the Poiseuille type.

We return to the porous sample. The porosity h of the sample is defined to be the volume of the pore space in a unit volume of the sample. We have $\mathrm{Re}[\sigma]=h(2\eta\omega\rho_2)^{1/2}/r$ for this case. Thus the quality factor for longitudinal motion is

$$Q_l=(r\rho/h)(\omega/2\eta\rho_2)^{1/2}. \tag{3}$$

We consider the case in which the pores are filled with liquid helium. The experiments performed by Jeffries *et al.* were carried out at temperatures below the lambda point of bulk He^4. However, a severe depression of the temperature of the lambda point has been observed in liquid helium which has been confined to fine pores.[8] In one case the temperature of the lambda point was observed to decrease from the bulk value of 2.18 to 1.36°K in a sample consisting of pores with a mean diameter of 43 Å. In the extremely fine pores which may result from the dehydration process it is conceivable that the temperature of the lambda point may be so greatly depressed that the liquid helium can be considered to behave as a normal viscous fluid throughout the temperature range of interest. We assume this to be so in the following calculations. Hence we take $\eta=30$ μP and $\rho_2=0.125$ g/cm³. If we assume a frequency of 10 kMc/sec, then $\omega=6.3\times10^{10}$ rad/sec. We also take $\rho=2$ g/cm³, $r=25$ Å, and $h=0.2$. Then $Q_l\cong230$.

If we assume sound propagates in the porous structure with a velocity of 2.5×10^5 cm/sec, the wavelength $\lambda=2.5\times10^{-5}$ cm. The penetration depth δ_l is given by

$$\delta_l=Q_l\lambda\cong5.8\times10^{-3}\text{ cm}.$$

For this case we find $(r/\Delta)\cong4$ so the high-frequency limit assumption is justified. For a frequency of 35 kMc/sec this penetration depth would be shortened by $(10/35)^{1/2}=0.54$. Penetration depths in the range of 10^{-2}–10^{-3} cm are obtained also from the phenomenological equations discussed in III. In Sec. III porous structures with pores of mean radii 5, 25, and 100 Å are considered and a frequency of 10 kMc/sec is used.

A similar estimate may be made for shear waves propagating through a porous medium. If we consider a slab of unit cross sectional area and thickness dx, the viscous retarding forces on the slab is

$$-h\eta(d^2v/dx^2)dx=h\eta k^2vdx,$$

where k is the magnitude of the wave vector. Hence $Q_s=\rho\omega/h\eta k^2$. We have $k=\omega/c_s$, where c_s is the velocity of propagation. Then

$$Q_s=\rho c_s^2/h\eta\omega^2.$$

With the same numbers used above we find

$$Q_s\cong2.2\times10^5$$

and

$$\delta_s=Q_s\lambda\cong4.4\text{ cm}.$$

Such an extremely large Q factor indicates that the porous layer would not be effective in relaxing the pure shear modes. However lanthanum double nitrate is a highly anisotropic crystal with C_{3v} symmetry. It may be shown that a pure shear mode exists only for wave vectors which lie in one of the vertical reflecting planes. The displacement associated with this shear mode is perpendicular to the reflecting plane.[9] All other modes contain an admixture of longitudinal and transverse

[6] See I. B. Crandall, *Theory of Vibrating Systems and Sound* (D. Van Nostrand Co., Inc., New York, 1962), Appendix A.

[7] See Ref. 6.

[8] K. R. Atkins, H. Seki, and E. V. Condon, Phys. Rev. **102**, 582 (1958).

[9] The existence of this shear mode may be understood by the following argument due to J. J. Hopfield. Let the y-z plane be a reflection plane and let **k** lie in the y-z plane. The wave vector **k** as well as the unit vectors y and z are left invariant by a reflection in the y-z plane. The unit vector $\hat{x}$ transforms into $-\hat{x}$ under this operation. Thus no mode can exist in which the displacement vector is a linear combination of $\hat{x}$ with $\hat{y}$ or $\hat{z}$. Since there are three normal modes and since the displacement vectors associated with any two of the modes must be orthogonal, a pure shear wave will exist corresponding to a displacement in the $\hat{x}$ direction.

motion. Thus, the layer will dissipate the energy contained in the longitudinal motion associated with a given mode. We can expect that almost all of the energy will be stored in modes which contain an appreciable admixture of longitudinal motion since the wave vectors associated with a purely transverse mode occupy only a vanishingly small fraction of the total solid angle in $\mathbf{k}$ space. Mode mixing upon reflection may also transfer energy from the dominantly transverse modes into the dominantly longitudinal modes.

III.

In this section we discuss in detail the phenomenological equations which describe propagation of longitudinal sound waves in a general porous structure with pores with fluid. Reflection of normally incident sound from a solid crystal-porous layer boundary will also be considered. The parameters relevant to the problem will first be defined. We have $h=$ the porosity, defined above, and $\beta=$the structure constant. The structure constant is rather difficult to define in a concise way and a bit of discussion is required.

Consider a sample described by a porosity h and a mean pore radius. In general the pore structure consists of a complex network of intertwining channels. If a pressure gradient is placed across the sample and if fluid is allowed to flow through the pores a certain volume per unit time will flow through the sample. Let dV_a/dt be this rate of flow.

If another sample with the same mean pore radius and porosity is constructed, but with all pores parallel to each other and also parallel to the pressure gradient, a volume flow rate $dV_b dt>dV_a/dt$ will be observed for the same pressure gradient. The structure constant is defined as the ratio

$$\left(\frac{dV_b}{dt}\bigg/\frac{dV_a}{dt}\right).$$

$P_1(x)$ is the force acting on the solid frame per unit area of the sample. $P_1(x)$ is not equal to the actual physical pressure on the frame, but is smaller by a factor of $(1-h)$. P_0 is the equilibrium pressure of the fluid. $P_2(x)$ is the excess force per unit area acting on the fluid. As above, $P_2(x)$ is not the actual excess pressure on the fluid, but is smaller by a factor of h. $v_1(x)$, $v_2(x)$ are the mean velocities of the fluid and frame, respectively. ρ_1 is the density of the material from which the frame is constructed. ρ_2 is the density of the fluid contained in the pores. B_1, B_2 are the bulk moduli of the frame and fluid, respectively. σ is the resistance constant. According to the above discussion, the effective resistance constant of a system of parallel pores is $h\sigma_0$, where σ_0 is the resistance constant of a single pore. If the structure constant $\beta\neq 1$, a given applied pressure gradient will result in a mean velocity reduced by a factor of $1/\beta$ compared to a parallel pore structure of the same porosity and pore size. Then the effective resistance constant is $\beta h\sigma$.

A set of four equations involving the variables P_1, P_2, v_1, and v_2 may be derived. Since the derivation of this set of equations is discussed in detail by Zwikker and Kosten,[10] the argument is not repeated here. If we define a constant

$$s=i\omega h\rho_2(\beta-1)+\sigma\,,$$

the equations of motion of the fluid and the frame as

$$-\frac{\partial P_1}{\partial x}=(1-h)\rho_1\frac{\partial v_1}{\partial t}+s(v_1-v_2)\,; \tag{5}$$

$$-\frac{\partial P_2}{\partial x}=h\rho_2\frac{\partial v_2}{\partial t}+s(v_2-v_1)\,. \tag{6}$$

The two continuity equations are

$$-\frac{\partial P_1}{\partial t}=B_1\frac{\partial v_1}{\partial x}-\frac{(1-h)}{h}\frac{\partial P_2}{\partial t}\,; \tag{7}$$

$$-\frac{\partial P_2}{\partial t}=hB_2\frac{\partial v_2}{\partial x}+(1-h)(B_2-P_0)\frac{\partial v_1}{\partial x}\,. \tag{8}$$

If plane wave solutions to (5)–(8) are assumed, the secular equation from which the wave vector may be found is easily derived. Let $\Gamma=k/\omega$ and let $\Sigma=s/i\omega$. The secular equation is then

$$\Gamma^4-\Gamma^2\left[\frac{h(1-h)\rho_1+\Sigma}{hB_1}+\frac{h\rho_2+\Sigma}{hB_2}+\frac{h(1-h)\rho_2+\Sigma}{hB_1B_2}\left(\frac{1-h}{h}\right)(B_2-P_0)\right]+\frac{h(1-h)\rho_1\rho_2+[(1-h)\rho_1+h\rho_2]\Sigma}{hB_1B_2}=0. \tag{9}$$

Equation (9) has two physically distinct roots, Γ_1 and Γ_2. The ratio of any two dynamical quantities may be computed for a given root of Eq. (9) by Eqs. (5)–(8).

$$\left(\frac{P_1}{v_1}\right)_{\Gamma_j}=W_{1j}=\frac{h(1-h)\rho_1\rho_2+[(1-h)\rho_1+h\rho_2]\Sigma+[h/(1-h)]\Sigma B_1\Gamma_j^2}{\{h\rho_2+[\Sigma/(1-h)]\}\Gamma_j}\,,$$

$$\left(\frac{P_2}{v_2}\right)_{\Gamma_j}=W_{2j}=\frac{h(1-h)\rho_1\rho_2+[(1-h)\rho_1+h\rho_2]\Sigma-[h\rho_2+\Sigma]B_1\Gamma_j^2}{[(1-h)\rho_1+(1/h)\Sigma-B_1\Gamma_j^2]\Gamma_j}\,,$$

$$\left(\frac{v_2}{v_2}\right)_{\Gamma_j}=\varphi_j=\frac{h(1-h)\rho_1+\Sigma-hB_1\Gamma_j^2}{h(1-h)\rho_2+\Sigma}\,.$$

[10] C. Zwikker and C. W. Kosten, *Sound Absorbing Materials* (Elsevier Publishing Co., Inc., New York, 1949), Ch. III. My notation differs slightly from that of Zwikker and Kosten.

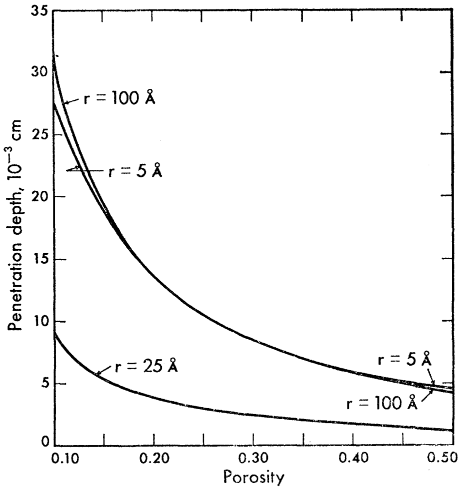

FIG. 1. Penetration depth of the acoustical mode as a function of porosity for various values of the mean pore radius.

The roots of Eqs. (9) have been obtained for values of h ranging from 0.10 to 0.50 and for pores with mean radii of 5, 25, and 100 Å. The fluid contained in the pores was assumed to be liquid helium in the normal state. The following numerical values were employed:

$$\rho_1 = 2.0 \text{ g/cm}^3$$
$$\rho_2 = 0.125 \text{ g/cm}^3$$
$$\omega = 6.3\times10^{10} \text{ rad/sec}$$
$$B_1 = 12.5\times10^{10} \text{ dyn/cm}^2$$
$$B_2 = 5\times10^{7} \text{ dyn/cm}^2$$
$$P_0 = 10^{6} \text{ dyn/cm}^2$$
$$\beta = 2.$$

We have $\sigma=\beta h\sigma_0$, where σ_0 is the single-pore resistance constant. For mean pore radii of 25 and 100 Å, $r/\Delta\cong4$ and 16, respectively. Thus we are in the high-frequency limit discussed earlier. For the case in which the mean pore radius is 5 Å, $r/\Delta=0.8$. Hence the flow is the Poiseuille type and we have used $\sigma_0=8\eta/r^2$ as the single-pore resistance constant.

The penetration depth $\delta_i=1/\text{Im}(\omega\Gamma_i)$. It is found that the penetration depth of one of the modes is exceedingly short. We denote the highly damped mode as Γ_1. The penetration depth δ_1 of mode Γ_1 is 9.5, 130, and 514 Å for the 5, 25, and 100 Å pores, respectively. This result is only weakly dependent on the porosity in the region $0.10\leq h\leq0.50$.

The penetration depth associated with the root Γ_2 is much longer and lies in the range of 10^{-2}–10^{-3} cm for $0.10\leq h\leq0.50$. A plot of the penetration depth of this mode versus porosity is given in Fig. 1 for the various pore sizes considered. The mode Γ_2 is found to propagate with a velocity in the range of 2.5×10^5 cm/sec in all cases considered. The ratios φ_1 and φ_2 were calculated for the two roots and it was found that $\varphi_1\cong-2.5\times10^3$ and $\varphi_2\cong0.50$–1.00. Hence the highly damped mode Γ_1 may be classed as an optical mode, since the fluid and frame oscillations are opposed in phase while the mode Γ_2 may be classed as an acoustical mode with the fluid and frame moving in phase.

The variation of the penetration depth of the acoustical mode with mean pore radius as shown in Fig. 1 is physically reasonable. From the expression for δ_l given in II, we expect

$$\delta_{100}/\delta_{25}=100/25=4$$

for a given value of h. For very small pores the fluid is dragged along with the frame and little dissipation occurs. Hence, the penetration depth is expected to increase.

Reflection of normally incident sound from a sharp crystal-porous layer boundary will now be considered. We assume a boundary with solid crystal filling the region $x<0$ and with a porous structure in the region $x>0$. It is assumed that the crystal and the material of which the frame is constructed may be described by the same density and bulk modulus. We refer to the region $x<0$ as Region I and the region $x>0$ as Region II.

If time dependence $e^{i\omega t}$ is assumed, the wave in Region I is described by the pressure $p^{\text{I}}(x)$ and velocity $v^{\text{I}}(x)$, where

$$P^{\text{I}}(x)=e^{ikx}+Re^{-ikx},$$
$$v^{\text{I}}(x)=(1/Z)(e^{ikx}-Re^{-ikx}),$$

and where Z is the acoustical impedance of the crystal.

In Region II, the force/unit area and velocity in the frame and fluid are given by

$$P_1^{\text{II}}(x)=Ae^{ik_1x}+Be^{ik_2x},$$
$$v_1^{\text{II}}(x)=A(1/W_{11})e^{ik_1x}+B(1/W_{12})e^{ik_2x},$$
$$v_2^{\text{II}}(x)=A(\varphi_1/W_{11})e^{ik_1x}+B(\varphi_2/W_{12})e^{ik_2x},$$
$$P_2^{\text{II}}(x)=A(W_{21}\varphi_1/W_{11})e^{ik_1x}+B(W_{22}\varphi_2/W_{12})e^{ik_2x},$$

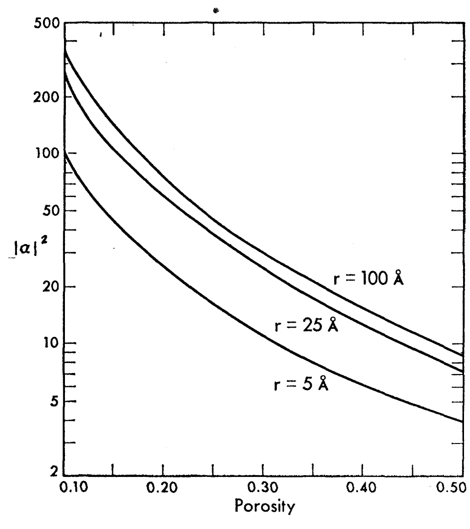

FIG. 2. The quantity $|\alpha|^2$ plotted as a function of porosity for various values of the mean pore radius.

where k_1 and k_2 are the wave vectors of the two modes of the porous structure.

The boundary conditions assume the following form:

(a) conservation of total force/unit area across the boundary

$$P^{\mathrm{I}}(0)=P_1^{\mathrm{II}}(0)+P_2^{\mathrm{II}}(0);$$

(b) continuity of pressure in the solid material

$$P^{\mathrm{I}}(0)=[P_1^{\mathrm{II}}(0)/(1-h)];$$

(c) continuity of velocity of the solid material

$$v^{\mathrm{I}}(0)=v^{\mathrm{II}}(0).$$

After employing the above boundary conditions, we find

$$B/A =\alpha=\left[1-\left(\frac{1-h}{h}\right)\left(\frac{W_{21}\varphi_1}{W_{11}}\right)\Big/1-\left(\frac{1-h}{h}\right)\left(\frac{W_{22}\varphi_2}{W_{12}}\right)\right],$$

and

$$R=(1-x)/(1+x),$$

where

$$x=[(1+\alpha W_{11}/W_{12})/(1+\alpha)]Z(1-h)/W_{11}.$$

The quantity $|\alpha|^2$ is a measure of the ratio of the energy contained in the acoustical mode to that in the optical mode and is plotted in Fig. (2) as a function of h for various values of the mean pore radius. The large values of $|\alpha|^2$ shown in Fig. 2 indicate that most of the transmitted energy is carried in the acoustical mode.

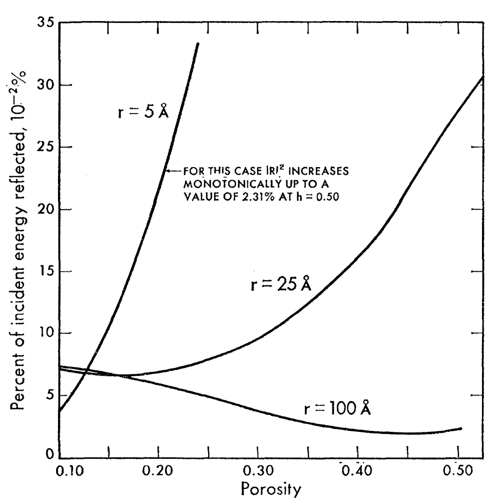

FIG. 3. The energy reflected from the boundary plotted as a function of the porosity for various values of the mean pore radius.

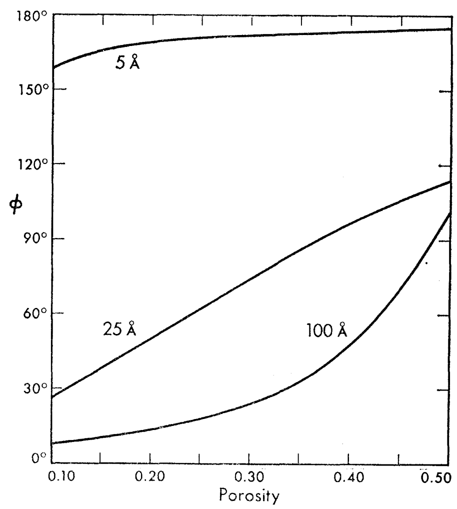

FIG. 4. The phase of the reflection coefficient plotted as a function of porosity for various values of the mean pore radius.

$|R|^2$ is the fraction of the incident energy which is reflected back into the crystal. $|R|^2$ is plotted in Fig. 3 while the phase of R is plotted in Fig. 4.

From Fig. 3 it may be seen that $|R|^2$ is so small that such a porous layer would be completely nonreflecting. In reality it is expected that the boundary between the solid crystal and the porous structure would not be sharp. A transition region would exist in which the porosity would vary smoothly from zero to some finite value. We expect that even less energy would be reflected from such a gradual barrier than from the sharp barrier assumed here.

If non-normal incidence were considered, the total energy reflected would be a function of the angle between the wave vector and the normal to the boundary plane. However, it appears probable that $|R|^2$ would be small over a large fraction of the solid angle, so that on the average only a small fraction of the incident energy would be reflected.

ACKNOWLEDGMENTS

I am indebted to Professor C. Kittel for suggesting the problem and for many stimulating discussions. I am also grateful to Professor C. D. Jeffries, Professor F. Reif, and Professor J. J. Hopfield for many helpful comments.