

MULTIPHONON INTERACTIONS AND THE THERMAL CONDUCTIVITY OF
CRYSTALLINE ARGON, KRYPTON, AND XENON

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Results obtained in an experimental investigation of the thermal conductivity of crystalline Ar (24–73°K), Kr (26–97°K), and Xe (26–120°K) are presented. An analysis of the temperature dependences of thermal resistivity in Ar, Kr, and Xe shows that multiphonon interactions in each substance make a significant contribution to the total thermal resistivity of the crystals. In reduced coordinates the thermal resistivities of all three solidified inert gases can be described by a single universal function of temperature.

MULTIPHONON interactions, which are understood to mean processes wherein more than three phonons participate, present one of the interesting problems of solid state physics. We know that in ideal dielectric crystals at temperatures above the maximum of thermal conductivity phonon interactions are the principal source of thermal resistivity. Although interactions of any order are possible in principle, it is customary to neglect multiphonon interactions even at temperatures close to a triple point.¹⁾ The important role of multiphonon interactions as a source of thermal resistivity in crystal lattices was first mentioned by Pomeranchuk,^[1, 2] who suggested that in some solids processes involving four phonons could be the principal phonon-scattering mechanism governing the thermal conductivity of a lattice. Despite the early date of this hypothesis the literature contains no unambiguous experimental evidence that multiphonon interactions affect thermal transport processes in solids. The insufficient accuracy of experimental measurements, and the existence in some cases of additional scattering and heat transfer mechanisms, prevent an accurate discrimination of thermal resistivity associated with multiphonon interactions. It is therefore extremely interesting to investigate thermal conductivity in solidified inert gases, which are the simplest solids. Because of the substantial experimental difficulties encountered in work with these objects there has been very little study of the thermal conductivity of solidified inert gases,^[5–7] except in the case of solid helium.^[3, 4] However, helium is not a suitable object because it crystallizes far below the Debye temperatures.

The present authors have previously shown^[8] that the results obtained from an investigation of solid argon can be accounted for by attributing a considerable role to four-phonon interactions. In the present work the investigation of this effect is extended to krypton and xenon crystals.

THEORY

We shall describe crystals of the solidified inert gases using the model of a face-centered cubic lattice central forces, and interactions between nearest neighbors. We shall consider the dependence of the four-phonon interaction on atomic mass and on the parameters characterizing the lattice and atom-bonding forces. A similar problem for three-phonon interaction was investigated in^[9]; the results of that work can be extended directly to our case. According to^[9], at sufficiently high temperatures the thermal resistivity of a cubic crystal in the presence of only three-phonon interactions, which arise out of third-order terms obtained when the potential energy of a crystal is expanded in powers of atom displacements from their equilibrium positions, can be represented by

$$W = C \frac{g^2}{f^3} \sqrt{\frac{m}{f}} aT, \quad (1)$$

where f and g are the second and third derivatives, respectively, of the interaction potential between atoms in their equilibrium positions, m is the atomic mass, a is the cubic lattice constant, and C is a dimensionless constant. In the first perturbation approximation, which was used to derive (1), the fourth-order expansion terms are responsible for four-phonon processes. The Hamiltonian of the lattice is then

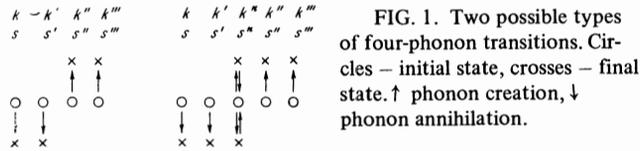
$$\hat{H} = \hat{H}_0 + \hat{\Phi}_3 + \hat{\Phi}_4,$$

where the sum $\hat{\Phi}_3 + \hat{\Phi}_4$, like Φ_3 ,^[9] can be regarded as a small perturbation of \hat{H}_0 . Without presenting the derivation of W (which resembles the derivation in^[9] using only three-phonon processes), we now turn to the final result obtained in calculating the thermal resistivity of a crystal at high temperatures:

$$W = W_{\text{III}} + W_{\text{IV}} = C \frac{g^2}{f^3} \sqrt{\frac{m}{f}} aT + D \frac{h^2}{f^4} \sqrt{\frac{m}{f}} kaT^2,$$

where W_{III} and W_{IV} are the thermal resistivities caused by three- and four-phonon processes, respectively, h is the fourth derivative of the interaction potential at equilibrium, k is Boltzmann's constant, and

¹⁾The relative role of multiphonon interactions is enhanced with increasing temperature.



D is a dimensionless constant. As anticipated, the inclusion of an additional phonon scattering mechanism is accompanied by an additional contribution to the thermal resistivity. It must be emphasized especially that in the presence of four-phonon processes the thermal resistivity of a lattice is a quadratic function of temperature in the high-temperature region.

When we consider the second perturbation approximation we easily determine^[10] that third-order terms in the expansion of the lattice potential energy also lead to four-phonon processes, which are effected via intermediate states having limited lifetimes. The two types of four-phonon interactions are compared schematically in Fig. 1. In the illustrated process two interacting phonons are annihilated and two others are created. Figure 1 shows that two variants of the second type of process are possible for given vectors \mathbf{k} and polarizations s of the created and annihilated phonons. In the first variant an intermediate phonon (\mathbf{k}^n, s^n) is created and then annihilated; in the second variant the phonon (\mathbf{k}^n, s^n) is annihilated and then created.

At high temperatures in the case of four-phonon processes associated with third-order terms, we have

$$W = C \frac{g^2}{f^3} \sqrt{\frac{m}{f}} aT + D' \frac{g^4}{f^6} \sqrt{\frac{m}{f}} kaT^2.$$

In the general case we have

$$W = C \frac{g^2}{f^3} \sqrt{\frac{m}{f}} aT + \left(D \frac{h^2}{f^4} + D' \frac{g^4}{f^6} + D'' \frac{hg^2}{f^5} \right) \sqrt{\frac{m}{f}} kaT^2. \quad (2)$$

Using the interaction potential^[11]

$$\varphi(r) = \varepsilon f(r/\sigma), \quad (3)$$

where ε and σ are a characteristic energy and length, we transform the last expression into

$$W = F \frac{\sigma^2}{\varepsilon} \sqrt{\frac{m}{\varepsilon}} T + G \frac{\sigma^2}{\varepsilon^2} \sqrt{\frac{m}{\varepsilon}} kT^2, \quad (4)$$

where the first and second terms describe the thermal resistivity that is associated with three-phonon interactions and four-phonon interactions, respectively. Therefore the ratio between three-phonon and four-phonon resistivity at a given absolute temperature is inversely proportional to the characteristic energy (which usually is taken as the interaction energy between two atoms at their equilibrium positions):

$$W_{IV} / W_{III} \sim kT / \varepsilon.$$

The dimensionless quantity kT/ε can be regarded as a reduced temperature T^* defined by the ratio T/T_{mol} , where $T_{\text{mol}} = \varepsilon/k$. Introducing $W^* = W/W_{\text{mol}}$, where $W_{\text{mol}} = (\sigma^2/k) \sqrt{m/\varepsilon}$,^[11, 12] the thermal resistivity of the lattice can be put into the form of a law of corresponding states:

$$W^* = FT^* + GT^{*2}. \quad (5)$$

The general form of W^* is obviously a polynomial in T^* whose degree is the order of the phonon interactions in the crystal.

In some cases, when the specific form of the potential function (3) is unknown it is convenient to use macroscopic lattice parameters—the Grüneisen constant γ and the Debye temperature Θ_D .

With the aid of the relations^[13]

$$\gamma \sim \frac{ga}{f}; \quad \Theta_D \sim \frac{\hbar}{k} \sqrt{\frac{f}{m}},$$

the thermal resistivity of the lattice in the presence of three- and four-phonon processes can be described by

$$W = Q \frac{\hbar^3}{k^2} \frac{\gamma^2}{ma\Theta_D^3} T + R \frac{\hbar^5}{k^4} \frac{\gamma^4}{m^2a^2\Theta_D^5} T^2. \quad (6)$$

This form of W can be used to analyze the results obtained for crystals that are not described by the adopted model. The parameter a can then be defined as the cube root of the volume occupied by a lattice-structure element of mass m . From (6) we obtain

$$\frac{W_{IV}}{W_{III}} \sim \frac{\hbar^2}{k} \frac{\gamma^2}{ma^2\Theta_D^2} T.$$

Using the Lindemann formula relating the melting point T to the Debye temperature,

$$T_m \sim \frac{k}{\hbar^2} ma^2\Theta_D^2,$$

the foregoing relation can be converted as follows:

$$W_{IV} / W_{III} \sim T / T_m, \quad (7)$$

where the square of γ is included in the proportionality coefficient. The exact computation of the last coefficient, even for the model that we have assumed, is a very complicated problem requiring a very fast computer. An approximate calculation for a face-centered cubic lattice with the Lennard-Jones potential yields a result of the order of unity. This indicates that four-phonon interactions have a substantial part in the generation of lattice thermal resistivity at high temperatures.

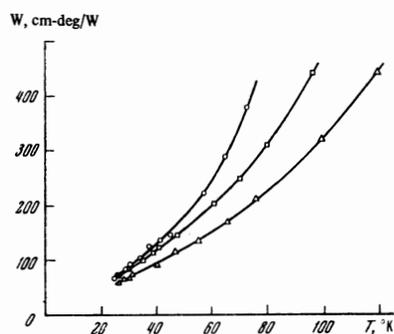
EXPERIMENTAL RESULTS AND DISCUSSION

The thermal resistivity of crystalline Kr (26–97°K) and Xe (26–120°K) was investigated using a stationary linear method with continuous visual monitoring of the specimens. A detailed description of the experimental technique has been published in^[14]. Measurements for both substances were performed on three polycrystalline samples, having 1–5-mm grains, which were grown from the vapor phase; the gases were at least 99.9% pure. All specimens were transparent and contained no visible defects. The maximum experimental error of the different runs fluctuated in the range 5–10%. Table 1 gives smoothed values of the thermal conductivity exhibited by crystalline Kr and Xe, along with our earlier values for solid Ar.^[8] The tabulated values were computed from analytic expressions having coefficients determined by least squares from the experimental data.

The literature gives no indication that the thermal

Table I. Thermal conductivity of crystalline argon, krypton, and xenon

T, °K	λ, mW/cm-deg			T, °K	λ, mW/cm-deg		
	Ar	Kr	Xe		Ar	Kr	Xe
25	14.3	15.0	18.1	75	2.55	3.52	4.78
30	11.4	12.1	14.5	80		3.16	4.36
35	9.23	10.1	12.4	85		2.83	3.98
40	7.59	8.53	10.6	90		2.55	3.65
45	6.45	7.33	9.22	95		2.32	3.38
50	5.49	6.38	8.12	100		2.09	3.10
55	4.69	5.60	7.21	105			2.85
60	4.03	4.94	6.43	110			2.66
65	3.46	4.40	5.81	115			2.45
70	2.98	3.93	5.26	120			2.23


FIG. 2. Temperature dependences of the thermal resistivities of crystalline Ar, Kr, and Xe. ○ — Ar, □ — Kr, Δ — Xe.

conductivity of solid Xe had been measured prior to the present work. The thermal conductivity of solid Kr was investigated by White and Woods,^[5] whose results agree with ours at the highest experimental temperatures, within the total experimental error limits. At low temperatures the results in^[5] are considerably lower than ours; at 26°K the discrepancy exceeds 30%. The disagreement appears to be associated with admitted defects of the specimens used in^[5]; the effects thereof should become manifest at low temperatures. Evidence is found in the fact that the thermal conductivity measurements for solid Ar that were obtained by White and Woods at low temperatures are also below our results^[8] and those given in^[7].

Julian's analysis^[15] shows that in solidified inert gases the thermal conductivity associated with three-phonon processes for $T > \Theta/4$ (where Θ is the high-temperature limit of the effective Debye temperature^[16]) is proportional to the absolute temperature. Table II gives values of Θ calculated using values of the parameters ϵ and σ in^[17] and a Lennard-Jones potential. Experimental Debye temperatures Θ_0 for $T \rightarrow 0^\circ\text{K}$ ^[18,19] are shown for comparison. It is seen from this table that we had investigated the thermal conductivity of solidified inert gases in the so-called "high-temperature" region, which is characterized in the case of three-phonon processes alone by a linear temperature dependence of the thermal resistivity.

Figure 2 shows the experimental thermal resistivities of Ar, Kr, and Xe as functions of the absolute temperature. It is noteworthy that the curves are considerably steeper than straight lines. We consider that this result is accounted for by the contribution of multiphonon processes to the thermal resistivity of solidified inert gases. In the case of Kr, and more especially Ar, it is not sufficient to take into account only the linear and quadratic temperature terms $C_{III}T + C_{IV}T^2$, which describe satisfactorily the temperature dependence of

thermal resistivity in Xe. It can be assumed that at the very highest temperatures phonon interactions of even higher orders than the four-phonon processes make some contribution to the thermal resistivity of Kr and Ar. If the observed temperature dependences of the thermal resistivities are associated only with the properties of the phonon interactions that occur in the crystals of solidified inert gases, the form of the law of corresponding states given in the preceding section should be fulfilled. Figure 3 shows that in the reduced coordinates W/W_{mol} and T/T_{mol} the experimental values obtained for all three solidified gases are described by a single universal function of temperature. The values of ϵ and σ given in Table II for the purpose of calculating W_{mol} and T_{mol} were borrowed from^[17] and had been used to calculate Θ .

In the case of Xe the smallness of the terms containing higher than the second power of T facilitates a quantitative comparison with the theory. The experimentally derived Xe coefficients, $C_{III} = 1.96 \text{ cm/W}$ and $C_{IV} = 1.04 \times 10^{-2} \text{ cm/deg-W}$ at $T = T_m$ yield $W_{IV}/W_{III} = 0.86$, which agrees well with our foregoing result. The value of C_{III} yields the proportionality factor $B_{exp} = 0.51 \text{ W/cm}$ in the dependence $\lambda = W/T$. From the equation

$$B = \frac{3}{10\pi^3} \left(\frac{k}{h} \right)^3 \frac{ma\Theta^3}{\gamma^2} \quad (8)$$

given in^[9] we obtain $B_{theor} = 0.66 \text{ W/cm}$ by using the values $\Theta = 56.7^\circ\text{K}$ (Table II) and $\gamma = 2.8$.^[20] In view of the crude assumptions used in^[9] to determine the numerical factor of (8), we must consider the agreement to be entirely satisfactory. The ratios W_{IV}/W_{III} at T_m that were obtained from the experimental data for Ar and Kr are close to the aforementioned ratio W_{IV}/W_{III} for Xe. It must be mentioned however that values of the coefficients C_{III} and C_{IV} were chosen somewhat arbitrarily to describe the thermal resistivities of Kr and

Table II

	ϵ [17], 10^{-16} erg	σ [17], 10^{-8} cm	ϵ/k , °K	$\frac{\sigma^2}{k} \sqrt{\frac{m}{\epsilon}}$, 10 cm-deg/W	Θ , °K	Θ_0 [18, 19], °K	B_{exp} , W/cm	W_{theor}^* , W/cm
Ar	165	3.41	120	534	85.1	93.3	0.46	0.60
Kr	230	3.65	167	751	64.8	71.7	0.45	0.59
Xe	318	3.92	230	922	56.7	64.0	0.51	0.66

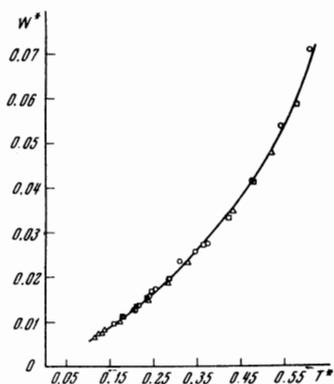


FIG. 3. Reduced thermal resistivity $W^* = W/W_{\text{mol}}$ of the three solidified inert gases versus reduced temperature $T^* = T/T_{\text{mol}}$. \circ - Ar, \square - Kr, Δ - Xe.

Ar, in view of the narrow temperature intervals within which higher than second order terms in T can be neglected as well as the limited experimental accuracy. However, it seems reasonable that, since the law of corresponding states was obeyed the given ratios should agree satisfactorily for all three solidified gases. For the reasons that have been discussed, it is expedient to recalculate the values of B for Ar and Kr from the corresponding value of B for Xe. The values of B_{exp} obtained in this way are given in Table II along with B_{theor} . B_{theor} was calculated with $\gamma = 2.8$.^[20, 21]

The fact that the reduced thermal resistivity does not depend on the quantum parameter $\Lambda^* = (2\pi\hbar/\sigma) \times \sqrt{m\epsilon}$ confirms the validity of Julian's^[15] expansion of the high-temperature thermal conductivity region. The results obtained for Ar indicate that $\Theta/4$ is a very plausible lower temperature limit for solidified inert gases.

We note in conclusion that the only literature concerning the influence of multiphonon processes on thermal conductivity consists of two experimental papers^[22, 23], which contain conclusions that require further verification, in our opinion. There is no basis for assuming that thermal conductivity is affected by multiphonon processes only in solidified inert gases. Unfortunately, the difficulty of computing the proportionality coefficient in (7) prevents a reliable prediction of the relative contribution made by these interactions to the thermal resistivities of other classes of solids.

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