

Scattering of phonons by dislocations in potassium

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(Received 23 March 1987)

Polycrystalline potassium samples have been plastically deformed under tension and the resulting effects on the phonon conductivity and phonon-drag thermopower have been investigated. The reduction of the lattice thermal conductivity λ_g due to dislocations is much larger than can be explained within the framework of phonon scattering by the static strain field of the dislocations. The phonon-drag thermopower entropy S_g is relatively weakly affected, a result which is consistent only with a model where different groups of phonons are primarily responsible for each of λ_g and S_g . The mechanism which limits λ_g in the unstrained (i.e., as cooled) K has not been isolated with certainty, but it seems unlikely to be dislocations.

I. INTRODUCTION

Some time ago we published the results of an investigation on the properties of potassium at low temperatures and high magnetic fields¹ (referred to as I hereafter). The effect of magnetic field \mathbf{B} on the thermal resistivity γ_{xx} was striking and resulted in a rapid increase in γ_{xx} , roughly as B^2 . We interpreted this as being caused by the lattice thermal conductivity λ_g , a deduction which has been supported by recent work.² Initial skepticism of the identification with λ_g (see Ref. 2 for a discussion) was due to the fact that earlier calculations³ had led us to expect a much smaller value of λ_g than was experimentally found, the difference being as much as a factor of 10 at 1.5 K. We ascribed the unexpectedly large λ_g to the unusually free-electron-like behavior of K which results in little or no interaction between electrons and transverse phonons. At liquid-helium temperatures it was assumed that phonon-phonon interactions [both N (normal) and U (umklapp)] are too infrequent to maintain equilibrium among the phonons, leaving the transverse phonons free to produce a large thermal conductivity. The earlier calculations had implicitly assumed that phonon-phonon processes maintain equilibrium, which results in a much lower conductivity.

A problem immediately arose that if phonon-phonon scattering is so weak, what mechanism finally limits the lattice thermal conductivity? There are various possibilities: (i) the residual phonon-phonon coupling might be sufficient to limit the mean free path of the transverse phonons, (ii) the residual non-free-electron character of K may be responsible (i.e., the presence of higher plane-wave components in the band structure), (iii) residual imperfections. In our previous calculations we chose the last option for simplicity of calculation. Since point impurities cannot provide sufficient scattering at low temperatures, we finally chose dislocations as the most likely imperfection. Using a result of Klemens⁴ for the scattering of phonons by dislocations, and assuming only phonon-electron [one orthogonalized plane wave (1 OPW)] and phonon-dislocation scattering as input to the calculations,

we found that a dislocation density of about 10^{14} m^{-2} was needed to fit our experimental results. This is many orders of magnitude higher than expected,⁵ which suggests either that the phonon-dislocation scattering is not well represented by Klemens's result, or that the mechanism which brings the transverse phonons to equilibrium had been incorrectly identified in I. This does not necessarily invalidate that work since one can treat the phonon-dislocation scattering as simply an approximate phenomenological representation of the residual scattering, whatever that might be.

The intent of the present work is to examine the effect of plastic strain, and particularly of dislocations, on the phonon conductivity and, to a lesser extent, on the thermopower of K. By this means it was hoped to clarify the above situation and gain more information about phonon-dislocation scattering in simple metals. Similar experiments have not been attempted before for the case of pure normal (as opposed to superconducting) metals; previous work on metals has been restricted to alloys or superconductors.⁶ In principle, the use of high magnetic fields to investigate phonon-dislocation scattering can be extended to many pure metals, but K provides an excellent first candidate in view of our experience with this metal.

II. THEORETICAL AND EXPERIMENTAL BACKGROUND

In this work the primary objective is to extract information about the scattering of phonons by dislocations. There are two models to describe this, the models being complementary rather than exclusive. In the first the phonons are scattered by the (static) strain fields of the dislocations. Many theoretical attempts have been made to calculate the magnitude of the scattering and all results are of the form

$$\tau_{pd}^{-1} = \Gamma N_d \omega = A b^2 N_d \omega, \quad (1)$$

where ω is the phonon frequency, Γ a parameter which determines the scattering strength and which is always proportional to the square of the Burgers vector \mathbf{b} , and

N_d is the dislocation density. The dimensionless constant A depends on the orientation of the dislocation, but we shall quote only values averaged over all orientations. All early theories were essentially single-parameter calculations, e.g., Klemens⁴ and Ziman⁷ found

$$A = \varepsilon\gamma^2 \quad (2)$$

where ε is a numerical parameter near unity (Ziman gives $\varepsilon \approx 1$, and Klemens, $\varepsilon \approx 0.6$), with γ being the Grüneisen constant. It should be noted that initial estimates of ε were about an order of magnitude lower,⁸ but the later estimates, as quoted here, are expected to be more reliable. Carruthers⁹ and Ohashi¹⁰ based their calculations on the third-order elastic constants. The former seem to be most appropriate to cases where central forces might dominate, and cannot readily be used to evaluate A for metals. That of Ohashi gives the relatively crude estimate of $A \approx \frac{1}{2}(c_{111}/c_{11})^2$, where c_{111} and c_{11} are a third- and second-order elastic constant, respectively. For Cu (Ref. 11) this yields $A \approx 1$ in rough agreement with Eq. (2) taking $\varepsilon \approx 1$ and $\gamma \approx 2$. However, for K, c_{111} is by far the largest third-order elastic constant¹² and results in $A \approx 40$, which is almost certainly an overestimate. More recently, calculations have appeared which use the third-order elastic constants more systematically. Brown¹³ gives a summary of these developments and using his own results has obtained agreement with experiments on Cu, Al, Si, and Ge, but not for alkali halides. For Cu, Brown finds $A \approx 11.6$ compared with Klemens's estimate of about 2.5, and for K one can use Brown's result (together with the experimental second-order¹⁴ and theoretical third-order elastic constants¹² to find $A \approx 6.0$, compared to Klemens's estimate, Eq. (2), of 0.86.

To summarize, the scattering of phonons by static dislocations should obey Eq. (1). The calculation of A has been refined to a point where one might have reasonable confidence in the numerical results. The recent calculations predict larger values of A than the earlier single-parameter theories, but the differences are less than an order of magnitude.

The second model is concerned with the possibility that phonons might also be scattered by vibrating dislocations.^{15,16} In some respects the dislocation behaves like a stretched wire which is more or less free to vibrate and which will scatter phonons inelastically. Because the dislocations will generally be pinned (by impurities or other dislocations), phonon scattering will be a maximum if the phonon drives the dislocation into resonance. Experiments^{6,17} on LiF below 1 K have provided the clearest evidence for this possibility. In particular, exposure of deformed LiF to γ radiation should produce more pinning and hence shift the resonance to higher frequencies; this would result in an increase of the lattice thermal conductivity (as is indeed observed), an increase which is not easy to explain by the static scattering model. Unfortunately the experiments on LiF have been complicated by the anisotropy of phonon-dislocation scattering; this is so extreme that some phonons appear to be only weakly scattered and tend to overwhelm the contribution of those most strongly scattered, so mask-

ing the effect to some extent. Nevertheless, it is not easy to understand the behavior of LiF for $T > 1$ K and indeed, Kneezel and Granato¹⁸ have been unable to obtain agreement between experiment and this dynamic scattering model for any $T > 0.1$ K, with discrepancies in magnitude of a factor of 30. Other ionic solids have been less extensively investigated,¹⁹ but the scattering appears to be more indicative of $\tau_{pd}^{-1} \sim \omega^0$ ($T > 1$ K) rather than Eq. (1). When the vibrational frequency of the dislocations is such as to produce a maximum in τ_{pd}^{-1} at very low temperatures, one expects $\tau_{pd}^{-1} \approx \omega^0 \rightarrow \omega^{-1/2}$ to be roughly appropriate at higher temperatures,¹⁵ a result perhaps closer to the experimental data than Eq. (1). Madarasz and Klemens²⁰ have recently used both static and dynamic mechanisms to produce good theoretical fits to the behavior of CuAl alloys. This is of particular interest in the present case because the vibrations of the dislocations will be damped by the conduction electrons and this must be included in the calculations.

Experimental results on the superconducting metals Nb and Ta have been used to support both models. Recent data on well-characterized samples deformed under tension²¹ are in good accord with Eq. (1) in both magnitude and frequency dependence, whereas earlier data on bent samples⁶ show maxima in τ_{pd}^{-1} which can only be understood with the dynamic model. These results are not necessarily in contradiction with each other; it may be that the type of plastic deformation is important, and also the quantity of dislocations introduced. Although these results are on superconductors so that electron damping of the dislocations will not be present, they are of interest to the present work because both are bcc metals and so are expected to exhibit large values of the Peierls-Nabarro stress. This is simply the stress required to move a dislocation from one lattice position to an equivalent neighboring position. Ge and Si would also have a high Peierls-Nabarro stress and these materials have already been mentioned as obeying Eq. (1). This should have the effect of strongly constraining the amplitudes of dislocation vibration, and also in increasing the resonance frequency. On the other hand, fcc metals have low Peierls-Nabarro stress, and thus comparisons between bcc metals (including K) and fcc metals should take this difference into account when dynamic scattering is envisaged.

Very recently Haerle *et al.*²² have studied the effect of plastic deformation on the electrical resistivity of pure potassium. They find some interesting behavior at $T < 1$ K which they ascribe to dynamic scattering of electrons by dislocations. At the moment it is prudent to treat this identification as tentative, but it does indicate that resistivity measurements might provide a useful complementary probe of these mechanisms.

It is clear from this brief review that the subject of phonon-dislocation scattering is still controversial and contains few clear answers. Because the theory of dynamic scattering is not as readily applied to specific materials as the static theory, the present approach will be to apply the latter in some detail to determine whether it provides a satisfactory explanation of the present data. The following provides a framework for later analysis and discussion.

The standard calculations of thermal conductivity^{4,7} show that λ_g can be written

$$\lambda_g = \frac{1}{3} \sum_i \int S_i(\omega) v_i^2(\omega) \tau_i(\omega) d\omega, \quad (3)$$

where the sum is over the three modes of polarization, $S_i(\omega) d\omega$ is the contribution to the specific heat of phonons in the range ω , $d\omega$, $v_i(\omega)$ their velocity, and $\tau_i(\omega)$ their relaxation time. If the Debye approximation is assumed, then

$$S_i(\omega) = \frac{\hbar^2 \omega^4 e^x}{2\pi^2 k T^2 v_i^3 (e^x - 1)^2},$$

where $x = \hbar\omega/kT$ and the other symbols have their usual significance. For scattering of phonons by the static strain field, Eq. (1) applies and if we substitute for τ into Eq. (3) and take the maximum value of X as X_m we obtain

$$\lambda_g = \frac{k^3 T^2}{6\pi^2 \Gamma N_d \hbar^2} \sum_i \frac{1}{v_i} \int_0^{X_m} \frac{x^3 e^x}{(e^x - 1)^2} dx. \quad (4)$$

By substituting τ directly, we make the assumption, following I, that N phonon-phonon scattering is relatively weak. If the opposite were the case the effective relaxation time of all phonons would be the same (at any T) and it would be more appropriate to insert this average value⁷ into Eq. (3). Providing the temperatures are low compared to the Debye temperature, the upper limit of the integral in Eq. (4) can be taken as ∞ , in which case the integral has the value of 7.21. Hence

$$\lambda_g = \frac{7.21 k^3 T^2}{6\pi^2 \Gamma N_d \hbar^2} \sum_i \frac{1}{v_i}. \quad (5)$$

When other scattering mechanisms are present the situation is more complex. In metals, phonon-electron scattering is strong and also gives the same frequency dependence as Eq. (1), i.e., $\tau_{pe}^{-1} \sim \omega$ and so λ_g has the same temperature dependence as Eq. (5). In this case, the lattice conductivity after straining will be reduced by the ratio $\tau_{pd}/(\tau_{pd} + \tau_{pe})$.

In principle a similar ratio is also appropriate to phonon-drag thermopower. Previous work has established that the thermopower of the alkali metals at low temperatures can be written²³

$$S = \alpha T + \beta T^3 + \gamma \exp^{-\Theta/T}. \quad (6)$$

The first term is identified with the diffusion contribution, the second with phonon drag due to the electron-phonon N processes, and the third with phonon drag due to electron-phonon U processes. The pure unstrained metal should exhibit the "full" phonon drag, i.e., when the phonon scattering is predominantly by electrons. Under these conditions²³

$$\beta = S_g / ne, \quad (7)$$

where S_g is the phonon entropy, n the number of electrons per unit volume, and e the negative electronic charge. Again, when another scattering mechanism with the same frequency dependence as τ_{pe} is introduced, then β will be reduced by the same ratio $\tau_{pd}/(\tau_{pd} + \tau_{pe})$ as found above for λ_g .²³ Hence from this point of view, the lattice thermal conductivity and λ_g contain similar infor-

mation. We shall delay further development and discussion until Sec. V.

III. EXPERIMENTAL TECHNIQUES

The recrystallization temperature of K is about^{24,25} 110 K so that any mechanical damage will rapidly anneal at room temperature, probably in a matter of minutes. For this reason the fundamental requirement is for a cryostat in which the relevant thermal properties can be determined in high magnetic fields, and which allows samples to be mechanically deformed at low temperatures. The straightforward techniques of deformation by tension was chosen because it has the useful attribute of allowing an estimate to be made of the dislocation density.

The samples were extruded through a circular stainless-steel die with a diameter of 4.4 mm, this being chosen so that any cross section has many crystallites (which were easily visible after storage and typically 1 mm in size). The lower end of the vertical sample was attached by split copper collars to the cold sink and the upper end by the same technique to a $\frac{1}{8}$ -in.-diameter thin-wall stainless-steel tube connected to a motorized puller at the top of the cryostat. The stainless-steel tube had thermal links to the helium bath at three separate points and also a simple sliding joint which ensured that no stress was applied to the sample during cooldown (except for the weight of a few inches of stainless tube and the heater assembly). Probes for the carbon thermometers and potential leads were threaded split copper collars about 2 mm long. Initially these were embedded in nylon supports but later models were self-supporting.

The cryostat was based on a design used previously²⁶ to measure the electrical resistivity of K at high B and is a double can arrangement with separate vacuum spaces. Normally the inner and outer cans are brought into good thermal contact using helium gas, but the inner sample space is under high vacuum to allow the thermal measurements to be made. The inner can can also be thermally isolated by pumping out the helium gas, and then raised to any desired temperature by electronic temperature controllers. In this way the sample can be deformed or annealed at whatever temperature is appropriate.

A series of measurements on one sample was typically as follows. The sample was extruded at about 30°C and left overnight or longer. It was mounted in the cryostat, the whole arrangement being inside a clean glove box in which freshly cut K samples could be kept for many hours without visible deterioration. After making the seal on the inner can, the cryostat was removed from the box, the outer can sealed in place, and the whole rapidly pumped to a high vacuum. The cryostat was cooled by radiation overnight to about 120 K, after which exchange gas was admitted to finish the cooling to 77 K and then to 4.2 K. After pumping out the inner can, a data set was taken under these initial conditions; this entailed measuring the thermal properties for both field directions for 0–6 T at five fixed temperatures in the range 1.4–4.2 K. The zero-field thermopower was also measured, and limited data on the electrical resistivity obtained (usually only at 1.2 and 4.2 K). At this stage the inner can was thermally

isolated and stabilized at a temperature convenient for plastic deformation (in the range 10–30 K). After this initial deformation (typically a strain $\epsilon \approx 0.005$ –0.01), the thermal properties were remeasured as above. This cycle was repeated for various strains up to 0.05–0.16 depending on the sample. The strain rate was about $4 \times 10^{-5} \text{ sec}^{-1}$ and the stress and strain were monitored²⁶ with an XY recorder; Fig. 1 is a typical example. Throughout this period the sample temperature never exceeded 30 K. Finally, the sample was annealed. For most samples this was done at 130–145 K for 15–30 min, but for the last sample (K5) a final anneal at 250 K was carried out. After each anneal the properties were remeasured.

In previous experiments²⁶ it was possible to find the effective form factor of the sample (l/A) by measuring the resistance at 12–16 K and comparing with published resistivity data. This was not possible here. The reason is simply that the potential and current wires to the sample were chosen for low heat loss as well as low resistance, which almost inevitably implies the use of superconducting Nb-Ti (the zero thermopower is also a useful attribute). However, Nb-Ti becomes normal near 9 K and then has a very high resistivity which prevents the operation of the superconducting chopper amplifier; previously Cu covered Nb-Ti leads were used so that high-temperature operation was possible. The following technique was therefore used to determine l/A . During plastic deformation the volume of the sample was assumed to be unchanged so that if it retains a uniform cross section, a change of l_0 to l (which is measured) implies a change in (l/A) of $(l/l_0)^2$. Comparison with previous data shows this to be an excellent approximation but there are also two simple checks which were made: (i) After making the correction $(l/l_0)^2$ to (l/A) and evaluating the resistivities ρ at 1.2 K and/or 4.2 K one expects to see a gradual rise in ρ due to the effect of dislocations. This was not visible in the low-purity samples, but was seen in samples K4 and K5. Thus for K4 the initial resistivity at 4.2 K, $\rho(4.2 \text{ K})$, was 2.27 n Ω cm, and 2.53 n Ω cm after a strain of 0.1. The difference of 0.26 n Ω cm is in good agreement with our previous values²⁶ of 0.25 n Ω cm. (ii) After annealing one expects $\rho(4.2 \text{ K})$ to return to its initial value. For sample K4 an anneal at 145 K for 30 min gave $\rho(4.2 \text{ K}) = 2.26 \text{ n}\Omega \text{ cm}$ in good agreement with the initial value.

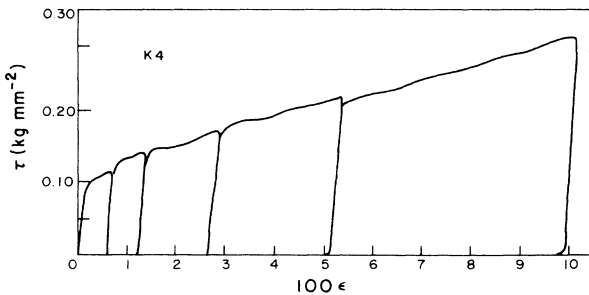


FIG. 1. The measured tensile stress τ as a function of strain ϵ for K4. τ has not been corrected for the thinning of the sample due to the strain. The breaks correspond to positions where the stress was removed and the sample properties measured.

These results suggest that the relative form factors are well known, probably to the level of $\leq 2\%$. They also suggest that the samples did deform uniformly, which was consistent with visual observations at the close of each series. However, the results were not accurate enough to be able to reliably obtain the change in $\rho(4.2 \text{ K})$ for small strains, a result which would have been very useful in determining the dislocation density as a function of strain.

Other experimental details were basically the same as described elsewhere.^{1,26}

IV. EXPERIMENTAL RESULTS

In I all independent thermal and thermoelectric coefficients were measured. The present arrangement does not allow the Righi-Leduc coefficient (γ_{yx}) nor the Nernst-Ettingshausen coefficient to be obtained. Thus to extract λ_g we resort to the results discussed in Ref. 27. For an uncompensated metal, as here, one finds that the measured thermal resistivity γ_{xx}^m is given by

$$\gamma_{xx}^m = \frac{\phi \gamma_{xx}^e + \lambda_g \gamma_{yx}^e}{\phi^2 + (\lambda_g \gamma_{yx}^e)^2}, \quad (8)$$

where γ_{xx}^e and γ_{yx}^e are the thermal resistivity and Righi-Leduc resistivity that the sample would have if $\lambda_g = 0$, and $\phi = 1 + \gamma_{xx}^e \lambda_g$. If we write $Y = (\lambda_g \gamma_{yx}^e / \phi)$, then Eq. (8) can be written as a power series in Y^2 , i.e.,

$$\gamma_{xx}^m = \frac{\gamma_{xx}^e}{\phi} + \left[\frac{1}{\lambda_g} - \frac{\gamma_{xx}^e}{\phi} \right] (Y^2 - Y^4 + \dots). \quad (9)$$

For $B \leq 6 \text{ T}$ the present data always satisfies $Y \leq 0.2$ and hence the series may be terminated at Y^4 with no significant loss of accuracy. Experimentally γ_{xx}^e is found to increase linearly²⁸ with B and so we write $\gamma_{xx}^e = a_0 + a_1 B$. It is also found that $\gamma_{xx}^e \lambda_g \ll 1$ under all conditions; in the worst case of the most impure samples in the deformed state, $\gamma_{xx}^e \lambda_g$ reaches a value of 0.03. This was ignored compared to unity so that Eq. (9) is finally written

$$\gamma_{xx}^m = a_0 + a_1 B + \lambda_g \gamma_{yx}^e - \lambda_g^3 \gamma_{yx}^e + \dots \quad (10)$$

Although γ_{yx}^e is not directly measurable, it has been shown in I to have the theoretical value of $L_0 T B / ne$ within the experimental error of about 2%, where L_0 is the Sommerfeld value of the Lorentz number ($2.445 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$) and $(ne)^{-1} = -44.5 \times 10^{-11} \text{ m}^3 \text{ C}^{-1}$ for K. In the actual analysis it was simply assumed that

$$\gamma_{xx}^m = a_0 + a_1 B + a_2 B^2 + a_4 B^4, \quad (11)$$

where the a_i are determined from least-mean-square fits to the data.

We expect a_0 to be essentially equal to the measured zero-field thermal resistivity, which was found to be so, typically to within 2–3% and often within 1%. In addition, a_2 and a_4 are not independent [cf. Eq. (10)] and should yield the same value of λ_g . In these experiments the ratio $-a_4 B^2 / a_2$ (i.e., Y^2) never exceeds 0.05 but even so, for the relatively unstrained samples, which have the highest λ_g , the λ_g calculated from a_4 was al-

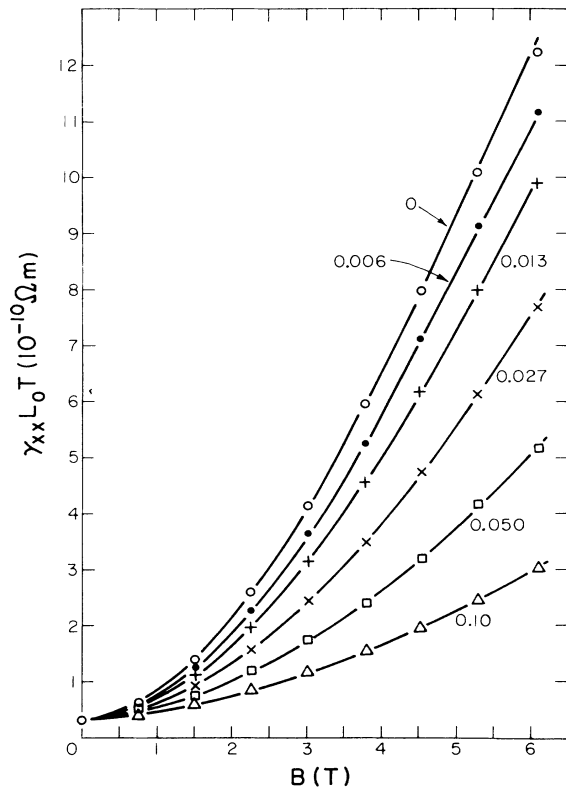


FIG. 2. Experimental results on the thermal resistivity γ_{xx} (multiplied by $L_0 T$) as a function of B for K4. The lines are fitted according to Eq. (11) and the strain is given on each curve. The temperature is close to 2.10 K for all data. Changes in γ_{xx} at zero field are not visible on the scale of this graph.

ways within 10% of that from a_2 . For the highly strained samples Y^2 drops to about 0.01 and the last term in Eq. (11) becomes negligible. It is concluded that Eqs. (8)–(11) fit the experimental data extremely well and that the values of λ_g so obtained are reliable. Figure 2 shows examples of the data and fitted curves. It should be noted that a_0 and a_1 are very insensitive to

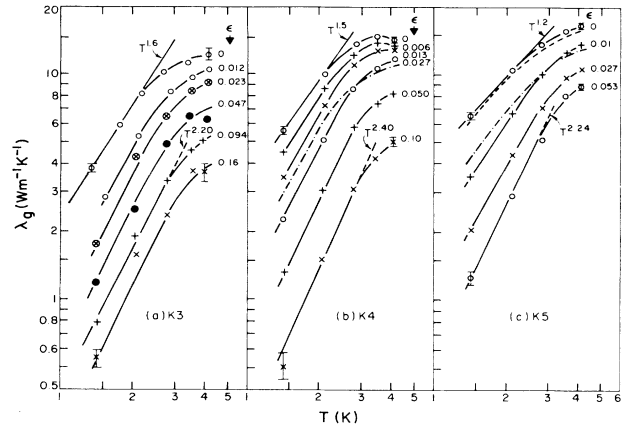


FIG. 3. The experimental data on the lattice thermal conductivity λ_g for samples K3, K4, and K5 for various plastic strains ϵ . The error bars are typical of all the data. Samples K1 and K2 were taken only at $\epsilon=0$ and ≈ 0.1 and are very similar to K3. The dot-dashed lines for K4 and K5 are results after an anneal at ≈ 140 K, and the dashed line for K5 is after an anneal at 250 K.

plastic strain, contrary to a_3 and a_4 . Figures 3(a)–3(c) give the results on λ_g for the three samples, K3, K4, and K5 (see Table I for resistance ratios of the various samples). Data for K1 and K2 were obtained only for strains of 0 and 0.1 and are not shown; they closely resemble K3.

Some features are immediately apparent from Fig. 3.

(i) Even low strains (≤ 0.01) produce a dramatic reduction in λ_g especially at low T . This sensitivity may explain the variability in λ_g that has been noted in various previous experiments. If the sample is constrained during cooling, then it is probably inevitable that there will be strain of the order of 0.01.

(ii) Purity is not a strong factor but it does seem to affect λ_g . In the unstrained samples λ_g is lowest for K3 (the most impure sample shown in Fig. 3) and highest for K5 (the purest). K1 and K2 were also of low purity and

TABLE I. Resistance ratios and thermoelectric parameters for unstrained and strained samples.

Sample	K1	K2	K3	K4	K5
$\rho(293 \text{ K}) \pm 5\%$	870	840	900	3630	5100
$\rho(1.2 \text{ K})$					
	Unstrained sample				
α (nV K $^{-1}$)		−13	−11	9	−0.5
β (nV K $^{-4}$)		−7.3	−7.8	−9.4	−12.2
$10^{-4}\gamma$ (nV K $^{-1}$)		2.0	2.0	2.6	3.0
θ (K)		15.6	15.5	15.9	15.2
	Strained sample				
α (nV K $^{-1}$)		−13		7	5
β (nV K $^{-4}$)		−4.6		−7.3	−10.0
$10^{-4}\gamma$ (nV K $^{-1}$)		1.1		1.9	2.5
ϵ		0.12		0.10	0.053

reproduce the low values for K3.

(iii) After deformation, an anneal at 140–150 K, which is well above the recrystallization temperature of about 110 K, is insufficient to return the sample to its initial condition [see K4 and K5 in Figs. 3(b) and 3(c)]. This is consistent with previous work on the electrical resistivity²⁶ where an extra resistivity of 0–0.05 nΩ cm always remained after such an anneal. Annealing at 250 K does return the sample to the original conditions. This reproducibility in λ_g might point to the residual phonon scattering mechanisms as being intrinsic to K.

(iv) K5 was deformed at 10 K so that the vacancies produced during deformation would remain in the sample.^{24,29} After taking results at a strain of 0.053 the sample was annealed at 20 K to remove the vacancies. Although previous work has shown that this causes a drop of nearly a factor of 2 in the resistivity induced by deformation, λ_g is unaffected within the accuracy of the experiments ($\approx 1\%$).

The zero-field thermopower was measured only for the samples in the unstrained and maximum strained conditions. Complete data are available for K2, K4, and K5 and these are shown in Fig. 4 along with curves fitted according to Eq. (6). Using the experimental Debye temperature of 90.6 K, β is calculated to be -9.0 nV K^{-4} which is to be compared with the average experimental value of $-9.2 \pm 2.2 \text{ nV K}^{-4}$. However, the experimental values

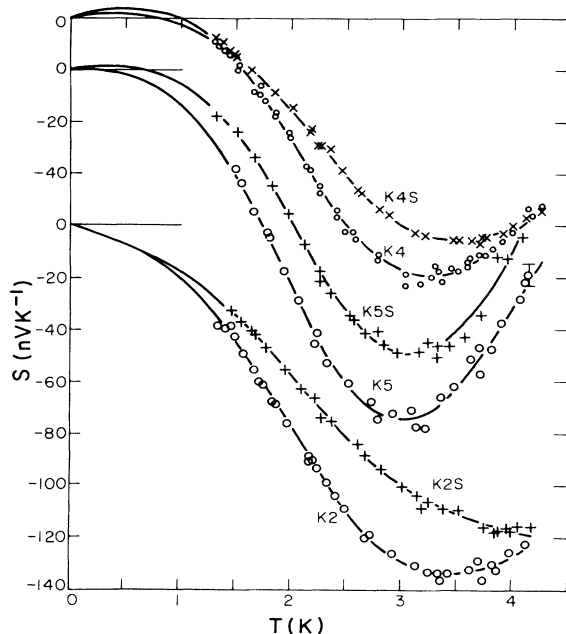


FIG. 4. The thermopower before and after straining for samples, K2, K4, and K5. The S signifies after straining which corresponds to $\epsilon=0.12$ (K2S), 0.10 (K4S), 0.053 (K5S). Absolute uncertainties should be about 2–3%. After the data for K5S were taken, the sample was annealed at 250 K. The results after this anneal are close to those of the unstrained sample being typically 5% lower in magnitude.

show a noticeable increase with purity; the absolute accuracy of the fits to the data is difficult to gauge and is probably about $\pm 10\%$, so at least some of this variation may not be real. The average result for Θ is $15.5 \pm 0.3 \text{ K}$ which is in poor agreement with the value of $23 \pm 2 \text{ K}$ quoted by Schroeder³⁰ for a related thermoelectric quantity, and about 20 K for the resistivity.³¹ The reason for this discrepancy is not known but the value of Θ does not vary strongly if the range of data is limited to lower temperatures (e.g., to $< 3 \text{ K}$). Equation (6) has also been fitted to the thermopower of the strained samples. Because γ depends sensitively on Θ when both are variables, the fitting was done by fixing Θ at the same value as obtained for the unstrained sample and allowing only α , β , and γ to vary. The quality of the fit is not significantly affected by this procedure. Table I collects all the coefficients. It is of interest that β and γ are reduced by about the same ratio in the strained sample, i.e., both N and U electron-phonon scattering are reduced by similar ratios.

We conclude this section by using the experimental data to estimate the dislocation density appropriate to these samples. There are two independent ways to do this: (i) using the electrical resistivity introduced by the dislocations and (ii) using the flow stress.

The resistivity increase (measured at 1.2 K) due to dislocations ρ_d is always about $0.25 \pm 0.05 \text{ n}\Omega \text{ cm}$ at a strain of 0.1 (see Sec. III). With Brown's estimate³² of $\rho_d/N_d = 8 \times 10^{-19} \text{ }\Omega \text{ cm}^3$ for K, we have $N_d = 3 \times 10^{12} \text{ m}^{-2}$. (Throughout this paper N_d refers to the dislocation line length per unit volume. Estimates made by etch pit counts are more appropriately referred to as the intersection density and for a random array will be factor of 2 lower than the volume density³³). Unfortunately the present data do not allow an accurate determination of ρ_d as a function of ϵ .

The second method relies on the fact that the flow stress τ due to dislocations is given by

$$\tau = r\mu b(N_d)^{1/2}, \quad (12)$$

where μ is the appropriate shear constant, b the Burgers vector, and r is a constant of about unity. (Recent results³⁴ give $N_d \sim \tau^{2.35}$ for Cu but for the range of N_d of interest this does not significantly affect our results). Data³⁵ on polycrystalline bcc Fe yield $r = 1.5$ when τ is the measured tensile stress and N_d the volume density. For K with $\mu = 1.2 \text{ GPa}$ (Ref. 36) and $b = 4.5 \times 10^{-10} \text{ m}$, together with the measured $\tau = 0.22 \text{ kg mm}^{-2}$ at $\epsilon = 0.1$, we have $N_d = 7 \times 10^{12} \text{ m}^{-2}$. It should be noted that τ is the flow stress measured after the initial sharp rise which is identified with the Peierls-Nabarro stress^{37,38} (see Sec. II). The difficulty in these experiments is that the low resolution on τ and ϵ does not allow the breakaway point to be established with accuracy, so again we do not have a reliable measurement of N_d versus ϵ , though by $\epsilon = 0.1$, τ is probably accurate to $< 20\%$.

If we take the mean value of the above estimates we have $N_d \approx 5 \times 10^{12} \text{ m}^{-2}$ at $\epsilon = 0.1$ which is probably reliable to about a factor of 2. We note that N_d is not expected to be a linear function of ϵ but will probably rise faster than ϵ .

V. DISCUSSION

It is apparent from Figs. 3(a)–3(c) that λ_g does not fit any simple power law over the whole range of T . However, if we evaluate the extra thermal resistivity W_d introduced by the deformation from $W_d = W_s - W_0$ where W_0 is the initial resistivity ($=1/\lambda_g$) and W_s that after plastic strain, then we obtain results shown in Fig. 5(a)–5(c). A simple power law $W_d \approx dT^{-c}$ now adequately fits the data where $c = 2.35 \pm 0.15$ for all samples, with no obvious purity or strain dependence of this exponent. Heavily deformed samples at low temperatures ($\epsilon \geq 0.1$) show $W_s \sim T^{-2.3}$ which is consistent with this result, i.e., W_d presumably dominates W_s here. If the exponent is set at 2.35, then the average value of the constant d for K1, K2, K3, and K4 at $\epsilon = 0.1$ is 3.0 ± 0.6 in m ks units.

The static strain field scattering of Eq. (5) predicts $W_d \sim T^{-2}$ which is only in fair agreement with these experiments. It is also possible to estimate the absolute magnitudes as predicted by Eq. (5) for comparison with the experiments. This is done by calculating $\sum_i 1/v_i$ using the measured elastic constants;¹⁴ the simple technique of averaging the v_i^{-1} along [100], [110], and [111] gives $\sum_i 1/v_i = 1.78 \times 10^{-3} \text{ m}^{-1} \text{ s}$. With $b = 4.5 \times 10^{-10} \text{ m}$, $A = 0.86$ or 6.0 according to Klemens and Brown, respectively (see Sec. II), and $N_d = 5 \times 10^{12} \text{ m}^{-2}$ as established in Sec. IV, then one finds

$$(W_d T^2)_K = 0.017 \text{ m K}^3 \text{ W}^{-1}, \quad (13a)$$

$$(W_d T^2)_B = 0.115 \text{ m K}^3 \text{ W}^{-1}, \quad (13b)$$

where the K and B refer to Klemens and Brown. If we take the best fits of the experiment to $W_d \sim T^{-2}$, the result is

$$(W_d T^2)_{\text{exp}} = 2.1 \pm 0.5 \text{ m K}^3 \text{ W}^{-1}, \quad (13c)$$

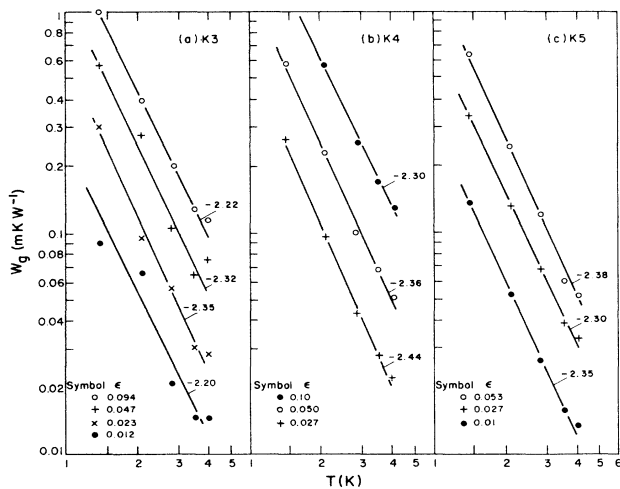


FIG. 5. The thermal resistivity W_d introduced into the samples as a result of plastic deformation ($W_d = W_s - W_0$ where W_0 and W_s are the resistivities before and after deformation). The slopes of the lines are shown, together with the strains ϵ .

i.e., about 2 orders of magnitude larger than Klemen's estimate and a factor ≈ 20 larger than Brown's estimate (which is probably the largest reliable value in the literature for static strain field scattering).

The above calculations are relatively crude and better estimates should be possible using the more-refined calculations of Leavens that appeared in I. The "real" phonon spectrum was used, in the first instance with electron-phonon scattering turned off, which makes the calculation equivalent to that above. From Fig. 15 (the dashed line) of I one sees that $W_d T^2 = 8.1 \times 10^{-3} \text{ m K}^3 \text{ W}^{-1}$ at $N_d = 5 \times 10^{12} \text{ m}^{-2}$. This is appropriate to Klemen's value of $A = 0.86$ and is about a factor of 2 lower than Eq. (13a); presumably the difference is due to the real spectrum and is probably caused by the strong anisotropy in the elastic constants of K. Equation (13b) will also be reduced by the same factor which aggravates the discrepancy between theory and experiment.

The analysis is still incomplete since we can only assume $W_d = W_s - W_0$ if both the dislocation scattering and the initial scattering mechanism have the same anisotropy and frequency dependence. (The problem is similar to that of deviations from Matthiessen's rule for the electrical resistivity). In metals W_0 is generally dominated by electron-phonon scattering, and this is probably true for the majority of the phonons in K. However, K is so free-electron-like that the purely transverse phonons along symmetry axes interact weakly, if at all, with the electrons and give rise to strong anisotropy of τ_{pe} . One normally assumes that phonon-phonon N processes tend to equalize τ_{pe} for all phonons but for K this would lead to a λ_g much smaller than observed; hence Leavens made the opposite approximation that these N processes play no role, at least at low T , and it is under these conditions that the solid curve in Fig. 15 of I was calculated, i.e., dislocation plus electron scattering of phonons without phonon-phonon N processes. Using this figure to find the appropriate N_d for the observed value of λ_g at $\epsilon = 0.1$ [$\lambda_g \approx (0.35 \pm 0.05) T^2 \text{ W m}^{-1} \text{ K}^{-1}$] yields $N_d = 1.0 \times 10^{15} \text{ m}^{-2}$. This again is appropriate to Klemens estimate of A and is in error by the same factor of 200 that was found above for dislocation scattering alone. Thus the result of more realistic calculations is that the right-hand side of Eqs. (13a) and (13b) should be reduced by a factor of 2 leaving discrepancies of 200 for Klemen's estimate and 37 for Brown's estimate. An alternate way of stating this result is that the experimental value of A is about 170, to be compared with the Klemens and Brown results of 0.86 and 6.0, respectively.

It is not possible to make a similar quantitative comparison for the case of dynamic scattering of phonons by dislocations. The original calculations of Granato¹⁵ predict a more rapid temperature variation for this mechanism with $\lambda_g \sim T^3 \rightarrow T^{3.5}$. This is a much higher exponent than the experimental result. Recently, Madarasz and Klemens²⁰ have made detailed calculations for Cu alloys taking both the static and dynamic mechanisms into account. Over the temperature range where dynamic scattering is strong (≈ 0.5 –10 K), λ_g is reduced by about an order of magnitude compared to static scattering. On the high-temperature side of the resonance, $\lambda_g \sim T^3$ in

agreement with Granato's calculation. If this was appropriate to K, then λ_g should show a pronounced change in slope at a temperature below the range available here. Of course Cu is fcc and K is bcc, and so the Cu calculation cannot be safely scaled for use in the present case.

Although the thermopower does not provide such a clear picture, it does complement the above analysis. Table I shows that the phonon-drag part S_g is relatively weakly affected in comparison with λ_g . It will be recalled from the discussion of Sec. II that S_g and λ_g are both reduced by the same ratio $\tau_{pd}/(\tau_{pd} + \tau_{pe})$, providing these relaxation times have the same frequency dependence and that τ_{pe} determines λ_g in the unstrained samples. The first assumption seems to be at least approximately obeyed since $W_d \sim T^{-2.35}$ implies $\tau_{pd}^{-1} \sim \omega^{0.65}$ which is close to the expected $\tau_{pe}^{-1} \sim \omega$. The second assumption is probably not true otherwise we should find $W_d \sim T^{-2}$ contrary to the experimental results. The variation of λ_g and S_g are consistent with the major assumption of I that λ_g is dominated by the contributions from the purely transverse phonons which interact only weakly with the electrons. Clearly S_g is dominated by all the other phonons, i.e., those which do interact strongly with electrons. When dislocations are introduced, the relative effect is greatest on the transverse phonons and so λ_g drops rapidly. On the other hand, the extra scattering caused by the dislocations to those phonons that are already effectively scattered by electrons is much smaller and so S_g is only weakly affected. Although calculations are not available for the variation of S_g with N_d for this model, one might expect that S_g will behave in a similar fashion to the phonon-drag part of the Nernst-Ettingshausen coefficient ϵ_{yx}^g which was calculated in I. (The comparison is actually closest with ϵ_{yx}^g rather than ϵ_{yx}^g/T as given in I). From Fig. 16 of I it will be seen that ϵ_{yx}^g/T decreases rather weakly with N_d . Even so these results on ϵ_{yx}^g/T indicate a stronger decrease than seen experimentally in S_g in the present experiments. The experimental results on λ_g at $\epsilon=0.1$ correspond to $N_d=1.0 \times 10^{15} \text{ m}^{-2}$ on Fig. 15 of I (see above); the actual number is not particularly significant since it varies with A and this value is used simply to reproduce the actual scattering observed in the experiments. For this same N_d , Fig. 16 of I shows that ϵ_{yx}^g/T is decreased to about 30% compared to the full phonon drag at $N_d=0$. By contrast the experiments show a smaller change with S_g reduced to about 75% of the initial value (cf. Table I for K4 in the initial and strained conditions).

There still remains the problem of what determines λ_g in the unstrained samples. The temperature dependence of λ_g is clearly not in agreement with that for W_d^{-1} (which is about $T^{2.35}$ over the whole temperature range), nor that appropriate to electrons W_e^{-1} ($\sim T^2$). Of course it is inevitable that phonon-phonon N processes will eventually bring the phonons into internal equilibrium³⁹ and so reduce the heat conductivity of the transverse phonons which are weakly scattered by electrons. This will result in a reduction of λ_g below that calculated for uncoupled phonons, which is in qualitative agreement with experi-

ments and remains the most likely mechanism near 4 K. However, even for $T < 2$ K, λ_g does not follow the temperature dependence expected for W_d^{-1} or W_e^{-1} but instead has a weaker power-law dependence $\sim T^{1.4 \pm 0.2}$ [see Figs. 3(a)–3(c)]. If residual dislocations are responsible for this low-temperature behavior, one would need a density of about an order of magnitude less than that appropriate to $\epsilon=0.1$, i.e., a density of roughly $5 \times 10^{11} \text{ m}^{-2}$ which seems unreasonably large⁵ and corresponds to a strain in excess of 1%.

The alternative, that the residual scattering is caused by electrons (due to the deviations from a single-OPW behavior) is more appealing at the moment. This would imply that the λ_g that is observed in the unstrained samples is close to an intrinsic property of K rather than being due to residual imperfections. Corbino experiments² have given lower and probably more irreproducible values of λ_g , which is consistent with the residual strain that one might expect with that arrangement. The present results on the purest samples are comparable with those taken on various other apparatus^{1,28} which introduce minimal strains suggesting an intrinsic property. This point might be worth pursuing in more detail, perhaps with the use of single-crystal samples.

Figures 3(a)–3(c) show that the peak in λ_g seems to be sensitive to sample purity. The effects of phonon-impurity scattering are readily included within the framework of Eq. (3). The relaxation time due to impurity scattering by mass difference effects is given by^{4,7}

$$\tau_{pi}^{-1} = \frac{\eta a^3 \omega^4}{4\pi v^3 G} \left[\frac{\Delta m}{m} \right]^2, \quad (14)$$

where η is the number of impurities per unit volume, a^3 the volume of a unit (primitive) cell, G the number of cells per unit volume, Δm the mass difference between host and impurity atoms, m the mass of the host atom, and v the phonon velocity. Adding τ_{pi}^{-1} to τ_{pd}^{-1} [Eq. (1)] and substituting in Eq. (3) gives [cf. Eq. (4)]

$$\lambda_g = \frac{k^3 T}{6\pi^2 \hbar^2 \Gamma N_d} \sum_i \frac{1}{v_i} \int_0^{x_m} \frac{x^3 e^x}{(1+yx^3)(e^x-1)^2} dx, \quad (15)$$

where $y = (\eta a^3 / 4\pi G v^3 \Gamma N_d) (\Delta m / m)^2 (kT / \hbar)^3$. Isotope scattering in K has $(\Delta m / m)^2 (\eta / G) \approx 2 \times 10^{-4}$, and this is also roughly appropriate to about 100 ppm of chemical impurity (i.e., similar to that expected in "pure" potassium). Taking $\langle v \rangle \approx 1.4 \times 10^3 \text{ m s}^{-1}$ as an average appropriate to the transverse phonons, $a = 4 \times 10^{-10} \text{ m}$ and $\Gamma = Ab^2$ with AN_d as appropriate to the measurements on unstrained samples ($\approx 10^{14} \text{ m}^{-2}$) gives $y = 3 \times 10^{-6} \text{ T}^3$; with this value of y the value of the integral is reduced only 1% at 4 K and therefore predicts no observable change in λ_g . The pure samples have a quoted impurity content of 300 ppm which would increase y by a factor of ≈ 4 . Furthermore, chemical impurities will cause strain field scattering, and possibly changes in the local interatomic forces such that, overall, y might be increased by an order of magnitude in the pure samples and possibly even more in the impure samples. Taking $y = 3 \times 10^{-5} \text{ T}^3$ reduces the integral by 10% and $y = 3 \times 10^{-4} \text{ T}^3$ reduces the integral by 40%, both at 4 K. These estimates sug-

gest that impurity scattering is not the primary cause of the reduction in λ_g near 4 K, but that there might be an observable difference between pure and impure samples, as is observed; this could only be verified by controlled experiments with impure samples. In this context the behavior of K5 is relevant since it was deformed at 10 K where the vacancies are immobile and remain in the sample.^{24,29} These vacancies produce an increase in residual resistivity of about the same magnitude as the dislocations introduced by the deformation, and will be about 5–10 % of the initial residual resistance. The vacancies were annealed out at 20 K but any change in λ_g was no more than 1% (which is the experimental limit on the relativity accuracy of λ_g); this is consistent with the above, that impurities have little effect in the pure samples.

Before leaving this section it might be useful to mention that the mean free path Λ of the phonons responsible for λ_g is readily estimated from the observed λ_g and the calculations in I, together with the fact that the $\tau^{-1} \sim \omega$ does give a roughly correct T dependence. For the unstrained sample one finds $\Lambda \sim 0.2/T$ mm which is an order of magnitude smaller than the crystallite size ≈ 1 mm.

VI. SUMMARY

These experiments have given a much clearer picture of the effects of dislocations on the lattice thermal conductivity and phonon-drag thermopower of K. Phonon scattering by static dislocations is unable to account for the magnitude of the observed changes in thermal resistivity; the experiments require a value of A in Eq. (1) of about 170 which is to be compared with Klemens's pre-

dition of 0.86 and Brown's of 6.0. Also, the temperature dependence of λ_g cannot be understood within this framework. There is insufficient information to be able to compare the experiments with the model involving inelastic phonon scattering by vibrating dislocations, but this is an obvious mechanism to investigate theoretically. The phonon thermopower S_g is only weakly reduced by dislocations, and samples which are not intentionally strained will probably show no visible effects. The strong reduction of λ_g and the weak reduction of S_g are consistent with the idea that different groups of electrons are basically responsible for each of these, as was put forward in I, but detailed discrepancies remain.

It has not proved possible to unambiguously identify the mechanism which limits the actual magnitude of λ_g in the pure unstrained samples in this temperature range, but the most likely involves residual scattering of the phonons by electrons due to departures from a single OPW band structure, combined with an onset of phonon-phonon U processes in the region of 3 K.

ACKNOWLEDGMENTS

Useful conversations with Dr. Z. S. Basinski and Dr. S. Saimoto are gratefully acknowledged. The help of Mark Roussel and Hugh deCourcy was also invaluable in completing this work. Professor J. R. Allen gave much useful advice and help with the calculation of various elastic constants. The work was carried out with a grant from the Natural Sciences and Engineering Research Council of Canada.

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