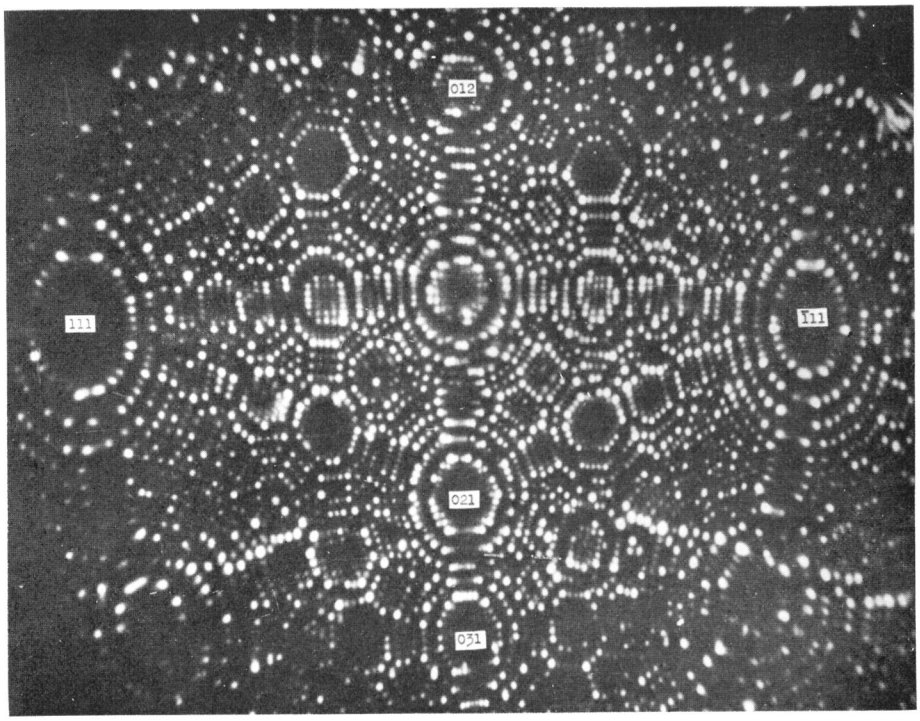

Fig. 12. Pt-50 % Co alloy crystal after ordering by annealing for 24 hours at 650°C. The (011) plane above the center is not marked so that the (111)-directed atom chains can be seen.

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The Study of Crystal Imperfections in Thermal Conductivity Measurements

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The aim of this evening lecture is to give a general survey over a field which has now become fairly extensive. There are many interesting problems in the subject, and one would wish to examine some of these in detail, but in the space of a single lecture one cannot possibly do more than mention the salient points. Even here a selection is necessary, and I hope that I may be forgiven when in some instances I have chosen items with which I am particularly familiar, because they have formed the subject of investigation by my own research group.

Before we can assess the use of thermal conductivity measurements for the detection of lattice imperfections, we must first examine those phenomena which we have to expect when no lattice defects are present, *i. e.* the scattering mechanisms and their temperature dependence in an ideally pure sample. Here we encounter the first difficulty, since the real specimens are never in this ideal state, but for most of the relevant cases the state of ideal purity has been approached closely enough experimentally to test the theoretical predictions. The simplest way to look at the problem is to consider our sample, which usually is a rod-shaped specimen through which heat is

made to flow longitudinally, as a hollow tube. Under a thermal gradient particles or quasi-particles are passing along this tube, and they will collide with such obstacles as they encounter on their way. The effect of these collisions, that is, the thermal resistance produced by scattering, is the subject of the theoretical and experimental investigation.

We will first discuss the case of the dielectric crystal which is generally simpler than that presented by a metal. Here the energy flow is made up of phonons, and the obstacles met by them are again phonons. The problem was treated theoretically by Peierls in 1929, who postulated that thermal resistance arises from collisions in which the phonon wave vector is not concerned and which are somewhat similar to Bragg reflections. These so-called "Umklapp" processes require a minimum energy of the order of $k\Theta_D/2$, where Θ_D is the Debye characteristic temperature. Thus the thermal resistance due to these collisions will decrease as the temperature is lowered, and it will depend on the nature of the lattice. A beautiful proof of the correctness of this theory was provided by measurements of the heat conductivity of solid helium by Wilkinson and Wilks. Normally it is not possible to change the Debye characteristic temperature appreciably but, owing to its high zero point energy, the compressibility of solid helium is so high that external pressure of less than 150 atm will change the value of Θ_D by 40%. The results yielded heat conductivity curves which rise steeply with falling temperature, and this rise is shifted to higher temperatures as the density of the solid is increased. For a perfectly pure dielectric crystal the heat conductivity should increase to infinity at absolute zero, if only the phonon-phonon interactions are considered. However, even if our hollow tube does not contain any scattering centres, phonons will be scattered on its walls. As was pointed out by Casimir, we must expect a resistance which in its mechanism is analogous to that of a Knudsen gas. Accordingly the thermal conductivity of the sample will fall to zero at absolute zero, and the temperature at which this drop sets in will be higher the smaller the specimen diameter is. This effect has, in fact, been found. Summarizing, we must expect the thermal conductivity of an ideally pure dielectric crystal to rise with falling temperature and, after passing a maximum, to drop to zero at $T=0$. These features are indeed borne out by the experiments.

Any extra scattering produced by lattice defects will reduce the heat conduction of the sample and the magnitude, as well as the temperature dependence, of this reduction provides the basis for the analysis of the number and nature of the defects. Since the wavelength of the thermal phonons increases with falling temperature, point defects are more effective as scattering centres at higher temperature, while close to absolute zero extended imperfections will be more effective. Since the early experiments by Eucken and Kuhn in 1928, the effect of impurities has been studied on a number of substances, and this work has been augmented lately by the study of irradiation effects. The latter has the advantage that the occurring changes can be studied step by step in the same specimen.

The theoretical analysis of scatter due to defects is largely due to the work of Klemens and that of Ziman. It shows that point defects will cause an additional resistance which, at low temperatures, is roughly proportional to the temperature, but which at higher temperatures becomes temperature independent. One of the reasons for this behaviour is the fact that at the lowest temperatures the dominant phonon wavelength is very large in comparison with the size of point defects, and the scattering is effectively Rayleigh scatter. This ceases to be the case as the temperature is raised and the scattering is becoming increasingly independent of the wavelength. Extended imperfections, such as dislocations, are relatively more effective at low temperatures since their size may be of the same order of magnitude as the phonon wavelength. Strictly, one must differentiate between the effect of the dislocation core and that of the surrounding strain field. It is the latter which extends far into the crystal, and which therefore is mainly responsible for the scatter of phonons. The theory agrees reasonably well with the experimental results, and it suggests *e. g.* that in the neutron irradiation experiments on quartz, carried out by Berman and his co-workers[1], not only point defects but also extended defects have been produced. As we shall see later, similar conclusions could be drawn from observations on superconductors.

Turning now to the work on metals, we have to consider energy transport, not only

by phonons but also by electrons. This makes the problem more complicated but, at least in the case of pure metals, there is a simplification due to the fact that the free electrons scatter phonons very strongly. This means that, in the first approximation, we can neglect the heat transport by phonons altogether, so that we need only examine the scatter encountered by electrons. Since electron-electron interactions are irrelevant, the only important contribution arises from the scatter of electrons on phonons. At low temperatures this leads to a thermal resistance of the form αT^2 which indicates that for the ideally pure metal crystal the heat conductivity should become infinite at $T=0$. Similar to the behaviour of dielectric crystals we must, at sufficiently low temperatures, expect scattering at the specimen boundaries, but this is a case which never arises in practice. Actually, even in the purest metallic samples, the electron mean free path is always limited by collisions with impurities which introduce a thermal resistance of the form β/T, resulting at the lowest temperatures in a heat conduction which rises from zero at $T=0$ linearly with temperature. We thus arrive for the thermal conductivity, K, of a pure metal at a curve which from absolute zero, rises at first linearly, passes through a maximum and then falls off again to higher temperatures, according to: $W=1/K=\alpha T^2+\beta/T$, where α is connected with Θ_D and β is a measure of the impurity content. The experimental evidence[2] shows that this simple assessment is quite satisfactory. It can easily be tested by plotting WT against T^3.

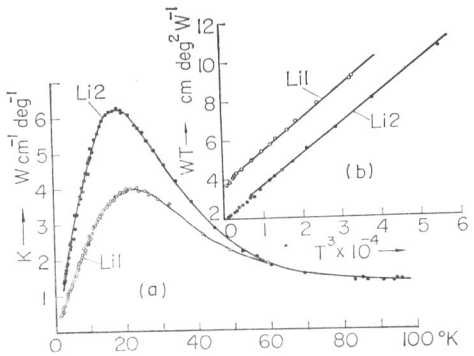

Fig. 1. (a) Thermal conductivity, and (b) WT/T^3 lines for two lithium specimens of different purity (after Rosenberg).

Owing to the short de Broglie wavelength of the electrons, β is essentially due to collisions with point imperfections and extended lattice defects are only effective in so far as they constitute series of point imperfections. While thus the thermal conductivity of a pure metal is a very sensitive detector of point defects, it can give little indication when these defects are arranged in a significant pattern. Moreover, since β is connected through the Wiedemann-Franz law with the residual electrical resistance, R_0, and the Lorenz number, L, as $\beta=R_0/L$, most of the information which can be gathered from thermal conductivity experiments can be obtained from measurements of the electrical resistance which are far less laborious. The situation is changed when we deal with an impure metal in which the electronic heat conduction is so much reduced by scatter on point defects that thermal conductivity by phonons becomes noticeable. For this much the same considerations are then applicable as have already been discussed in the case of the dielectric crystal. Experiments on a number of alloys have in this way led to the determination of dislocation densities in these specimens.

The thermal conductivity of metals which become superconductive is of special interest in the detection of lattice faults. The first deter-

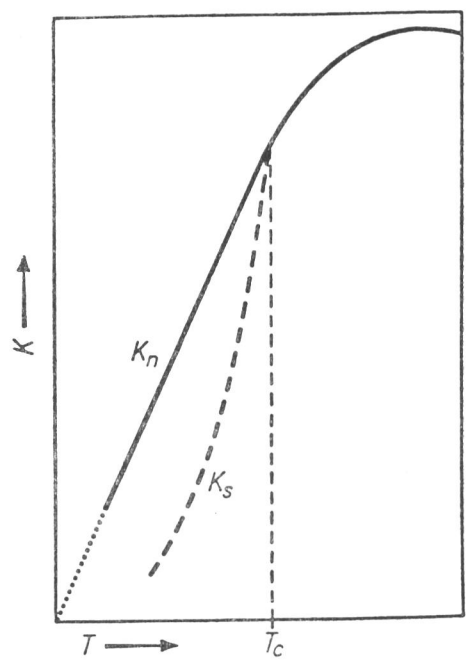

Fig. 2. Thermal conductivity of a metal (- - -) in the superconductive, and (——) in the normal state. The electrical resistance disappears at T_c.

mination was made in 1912 by Kammerlingh Onnes, but the result appeared to him at the time so unlikely that it was not published until several years later. It appears that at the same temperature, T_c, at which the electrical resistance vanishes suddenly, the thermal conductivity begins to drop below the value for that in the normal state. A comparison between the two values is quite easy since the normal state can always be restored by the application of a relatively small magnetic field which has no appreciable effect on other properties of the metal. We must thus distinguish, at any temperature below T_c, between the two values of the thermal conductivity; K_s in the superconductive and K_n in the normal state. For pure metals, K_s is generally smaller than K_n which, while surprising at first sight, is exactly what should be expected. Since superconductivity indicates a cessation of energy exchange between electrons and the crystal lattice, the electrons thus affected cannot contribute any more to the process of thermal conduction. As the fraction of conduction electrons passing into this state of lower energy increases gradually as the temperature is lowered below T_c, the ratio of K_s/K_n which is 1 at T_c becomes accordingly smaller. Since the rate at which electrons pass into the lower state with falling temperature can be estimated from experimental data, a semi-empirical relation between K_s/K_n and temperature can be deduced which is not strongly dependent on the theoretical model employed. This curve, which is usually plotted against the reduced temperature T/T_c, provides a measure of the reduction of electronic heat conduction when the metal becomes superconductive.

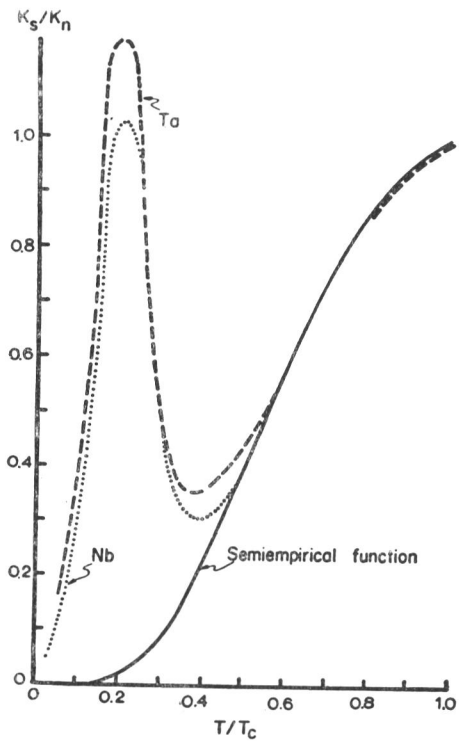

Fig. 3. The semi-empirical function for K_s/K_n plotted against the reduced temperature T/T_c, and the experimental data for tantalum and niobium single crystals.

For certain crystals, as, for instance, tantalum and niobium, the semi-empirical function seems to provide a good description of the experimental results as long as temperatures $T/T_c > 0.5$ are considered. However, below this temperature deviations occur which are very striking, and which even lead to values of K_s/K_n in excess of 1. The reason for the failure of the theory is that it only takes into account electron conduction. However, as the conduction electrons gradually disappear from the thermal distribution, they not only cease to transport heat, but they also cease to act as scattering centres for the phonons. Consequently, we must expect, particularly in a pure single crystal, a large phonon conductivity to make its appearance.

In order to test this hypothesis, experiments were carried out in which lattice defects of different nature were introduced into the specimens, and their effect on both K_s and K_n was recorded. It could be shown very clearly that strain, which causes dislocations, will reduce the observed maxima in K_s, whereas K_s will remain largely unaffected at the lowest temperatures by the introduction of impurities. Conversely, K_n is much reduced by the addition of impurities, but is highly insensitive to strain. These tests not only showed that the heat conductivity maxima in the superconductive state are due to phonon conduction, but they also pointed to a field of practical application. Since K_s is largely sensitive to dislocations and other large scale imperfections, whereas K_n records selectively the point defects, measurements on the same specimen in both the superconductive and the normal state will allow separate assessment of each. The method requires the use of low temperatures, but it has the great advantage that the two

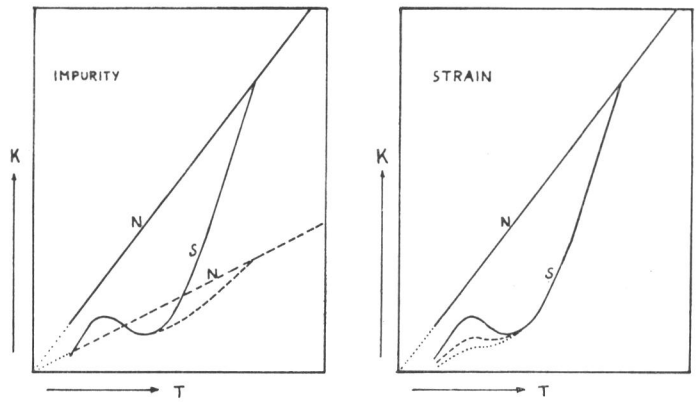

Fig. 4. Diagram showing the effects of impurity and strain on the thermal conductivities in the normal and superconductive state.

types of defect can be determined independently without change in the physical state of the specimen.

Experiments have been made on samples of several metals, investigating the production of dislocations by stretching and bending as well as the effects of subsequent annealing. Comparison with theory has yielded in some of the cases a surprising degree of agreement and, in view of these encouraging results, the method has, in the last few years, been applied to the assessment of the effects of neutron irradiation. This type of damage is not as yet fully understood and, owing to the extensive damage caused by each neutron, difficult to assess. It is clear that a method which is capable of differentiating between small and large-scale lattice disturbances is particularly useful in helping to elucidate the processes involved.

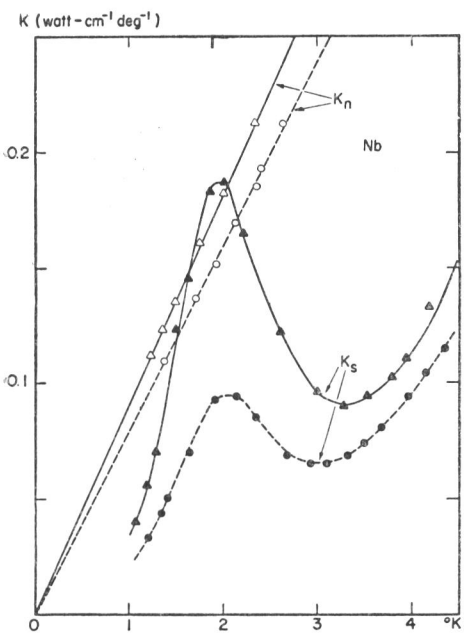

Fig. 5. Thermal conductivity of a niobium single crystal in the normal and superconductive states before (——) and after (- - -) neutron irradiation.

In one experiment[3], the thermal conductivities K_s and K_n of a niobium single crystal were measured first in the undamaged state, and then again after the specimen had been subjected to neutron irradiation in a research reactor at operating temperature. Both K_n and K_s were found to be reduced, indicating the creation of point imperfections as well as of extended defects. Under the conditions of the experiment it could be assumed that, while the interstitials could migrate easily, the vacancies remained in place. The results could therefore be interpreted as follows: The vacancies, being point imperfections, are responsible for the reduction in K_n while the interstitials migrate to form small dislocation loops or jogs on existing dislocation lines. A plausible estimate led to an increase of the order of 10^9 dislocations per cm² to be expected as the result of irradiation, while an analysis of the reduction in K_s yielded 3×10^9 lines per cm². This agreement is a bit too satisfactory to be accepted without reserve, and more work on these lines must show whether or not it was fortuitous. However, the method seems to show good prospects for the assessment and interpretation of complex lattice defects.

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