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Phonon scattering at crystal surfaces

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Through measurements of the low-temperature (0.06 – 2.0 K) thermal conductivity of dielectric crystals in the boundary-scattering regime we are searching for causes of diffuse phonon scattering by crystal surfaces. Thin (≤ 100 Å) gold films on polished sapphire surfaces cause diffuse phonon scattering above 0.3 K. Below that temperature, specular reflection again begins to dominate. The same diffuse scattering can be caused by implantation of Xe ions which damage a layer $\simeq$500-Å thick underneath the sapphire surface. For gold films, the effect diminishes with increasing thickness, i.e., greater perfection of the film. Because of the very small thickness of the layers in which the diffuse scattering occurs the phonon-scattering strength must be very much stronger than any phonon scattering previously observed in the bulk of dielectric crystals. Several potential explanations are discussed. However, none appear to be sufficiently general to account for both kinds of surface treatments.

I. INTRODUCTION

When elastic waves hit a surface, they can be reflected or they can be diffusely scattered. Diffuse scattering will lead to Casimir boundary scattering in thermal conductivity,[1] and is also expected to result in a reduction of the Kapitza resistance between two media below the value predicted on the basis of the acoustic impedance mismatch.[2] By roughening the surface of dielectric solids through sandblasting or abrading, the diffuse phonon scattering can be enhanced,[3] and it has been shown that such treatments lead to perfectly diffuse scattering, i.e., quantitative agreement between the measured thermal conductivity and the Casimir theory.[4,5]

The origin of the diffuse phonon scattering is poorly understood and the question we wish to address in this study is whether the diffuse scattering arises by the rough surface itself, or by the damaged layer underneath the surface (which contains high dislocation densities to considerable depth), as has been suggested in several earlier studies although a clear distinction between the two effects was not possible.[4,6] In addition, our study will deal with the broader question of phonon scattering by defects in the vicinity of crystal surfaces, and will thus extend the much explored subject of the influence of lattice defects in the interior of crystals on their thermal conductivity to defects on or near crystal surfaces. We will show that such surfaces defects can cause phonon scattering which is far stronger than is known for volume defects.

In deriving his formula Casimir[1] assumed that the phonons will also be thermalized during the collision with the surface, i.e., the spectral distribution of the scattered phonons will be characteristic of the temperature of the surface elements by which they were scattered. It is not clear whether this point has also been proven by the earlier experiments. Conceivably, the conversion from a phonon flux to an effective temperature occurs predominantly in the thermometers. Our work will not resolve this question either; however, since the temperature differences between the two ends of our samples always were relatively small, the deviations from thermal equilibrium in the phonon spectrum also could not be large, and hence we will ignore this complication for the time being.

II. EXPERIMENTAL APPROACH

Thermal conductivity was measured on undoped sapphire crystals grown by flame fusion. The cylindrical samples, 5 mm in diameter and 50-mm long, had polished surfaces which appeared optically smooth (supplied by Fa. Wild in Idar-Oberstein, Federal Republic of Germany, from crystal boules produced by Fa. DJEVA, Monthey, Switzerland). Heat flow was along the crystallographic *c* axis.

One form of surface damage chosen was ion implantation. Xenon ions were implanted at room temperature using the Jülich 400-kV ion implanter.[7] With an ion-beam energy of 350 kV, a damaged layer estimated to 500 Å thick was produced underneath the polished sapphire surface,[8] with an integrated flux of 5×10^{15} ions/cm^2. The exact depth of damage is difficult to estimate, since the ions had to penetrate a gold film of ~100 Å, the thickness needed to bleed off the charges from the electrically insulating crystal. Through sputtering, the thickness of the gold film decreased during the implantation process. The estimate of the thickness of the damaged sapphire layer is therefore thought to be accurate only within ±150 Å. While at integrated fluxes greater than 10^{17} ions/cm^2, blistering and spallation has occured in previous experiments on sapphire,[9] no such damage was observed with the integrated fluxes used in our experiments, and the polished faces appeared as smooth after the irradiation as before. Hence, this treatment resulted in disorder in a thin layer underneath the surface, without, however, roughening it. It thus allows separation of surface roughness from disorder in the volume next to it.

Another form of surface treatment used was evaporation of thin gold films onto the polished crystals. These films were found to be very delicate and could be wiped off easily. In preparation for the evaporation, the crystals were cleaned for 10 min in an ultrasonic bath in a saturated solution of $K_2Cr_2O_7$ in H_2SO_4, rinsed in triply distilled water and dried in air. Prior to the evaporation of gold in a vacuum of 10^{-8} Torr onto the sample held at room temperature, it had been further cleaned through a vacuum bakeout at 200 °C. Such a bakeout will remove some, although certainly not all, of the water that normally adheres to sapphire surfaces.[10] For example, on fine powders of Al_2O_3, a 12-h outgassing at 150 °C has been found to leave approximately half a monolayer of H_2O on the grains; at $T=1000\,^{\circ}C$, hydroxide ions have still been observed to come off.[11] The thickness of the gold film was determined by the frequency shift of a quartz thickness monitor. Surface roughening was done with a water-cooled beltsander, since sandblasting did not affect the surface.

Thermal conductivity was measured between 0.06 and 2.0 K, using a standard steady-state technique recently reviewed elsewhere.[12] The temperature scale was the one used and tested at Cornell University.[12,13] As a control of the equipment used, one sample was measured both at Jülich and at Cornell.[14] The results were found to agree, as will be discussed below.

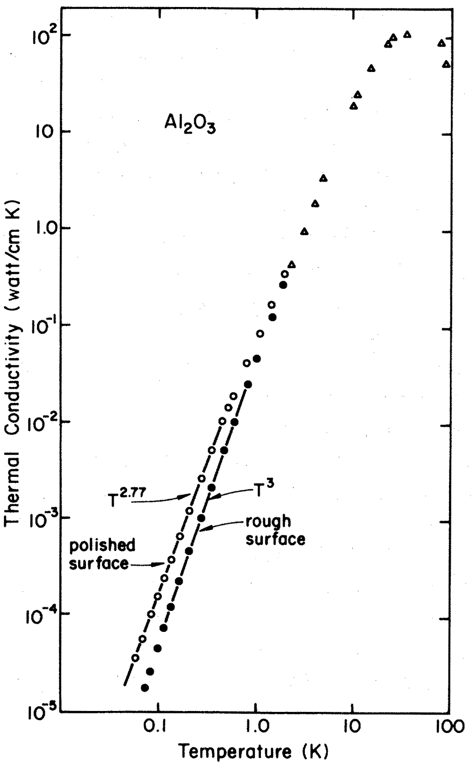

FIG. 1. Thermal conductivity of sapphire single crystals. Open triangles (Ref. 3) denote the conductivity of 2.52 mm diameter, flame-polished sample. Open and closed circles, in this study, represent the conductivity of the sample as described in text, 5 mm diameter. The $T^{2.77}$ line through the data for the polished sample is a good fit, while the T^3 line through the data on the surface-roughened sample is the Casimir prediction (not considering phonon focusing), and is not a good fit, as is seen in Fig. 2, where both sets of data are plotted as Λ/T^3, using the same symbols. For the determination of Λ_{Casimir}, we used the measured specific heat of sapphire, $C_v=2.86\times10^{-8}T^3$ J/g K [R. Q. Fugate and C. A. Swenson, J. Appl. Phys. 40, 3034 (1969)]. Mass density $\rho=3.98$ g cm^{-3}. From these data, $v_{\text{Debye}}=7.12\times10^5$ cm sec^{-1} and $\Lambda=8.12\times10^{-2}T^3l$ (W cm^{-1}K^{-1}), with T in degrees K, has been calculated, where l is the average phonon mean free path ($l=d$ for a cylindrical sample in the Casimir theory). Dominant phonon wavelength (Ref. 18) for Al_2O_3 is 4×10^3 Å at 1 K, and varies as T^{-1}.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The thermal conductivity measured on a sample with a roughened surface agrees well with earlier measurements on sapphire crystals,[3,15,16] as shown in Fig. 1. The conductivity of the polished sample is larger than that measured on the sample after its surface had been roughened. The data also indicate an increase of specular reflection with decreasing temperature, i.e., increasing phonon wavelengths, as is known to occur. The difference between polished and rough surface, however, is smaller than for other crystals, e.g., for LiF, where specular reflection extended all the way to the thermal conductivity maximum at ~15 K, and where the conductivity of the polished and annealed sample at 1 K was found to be over five times larger than that of the sample after sandblasting.[4] Conceivably, phonon scattering by bulk defects, or by residual surface roughness of the polished sample, are responsible for the relatively smaller effect of surface polish on the sapphire.

In order to demonstrate more clearly the difference produced by the different surface treatments, we will show the data in the following as thermal conductivity Λ divided by T^3, the cube of the temperature. The upper and the lower curves in Fig. 2 are the same data as those shown in Fig. 1. According to the Casimir theory, completely diffuse scattering on the rough surface would lead to a phonon wavelength- (i.e., temperature-) independent phonon mean free path equal to the sample diameter, in our case 0.5 cm. The experimental mean free path, shown on the right-hand ordinate of Fig. 2, is close to that predicted value, although not quite temperature independent. This is not an experimental error, because the same data were obtained when the sample was remeasured at Cornell. It is unlikely to be an artifact resulting from an error in our temperature scale, which has been used at Cornell for many years and which has resulted in data of specific heat and thermal conductivity in good agreement with the theoretical predictions[17] (Debye T^3 law and Casimir mean free path, respectively). Most recently, the conductivity of a high-purity silicon crystal with sandblasted surfaces has been measured at Cornell under identical conditions,[14] yielding a temperature-independent mean free path which agreed with the Casimir mean free path predicted by McCurdy *et al.*[5] (whose calculation included the effects of phonon focusing). Hence, we conclude that the mean free path observed on the sapphire sample with a roughened surface shows the diffuse scattering by some bulk defects in addition to that by the rough surface. Phonon focusing is also likely to affect the magnitude of the predicted Casimir mean free path.

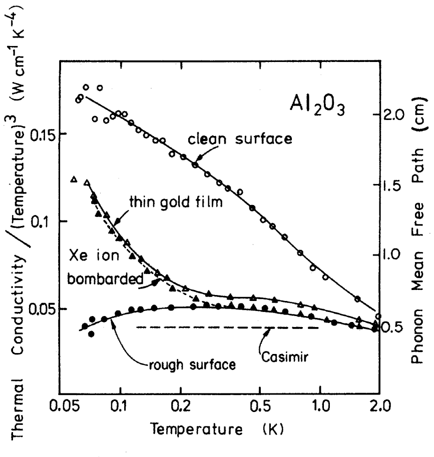

FIG. 2. ΛT^{-3} for one Al_2O_3 single crystal. Phonon mean free path computed with information given in caption of Fig. 1. Open and closed circles denote the same data as presented in Fig. 1. Open triangles represent a path for a gold film of 50-Å average thickness. Closed triangles denote the path after Xe ion implantation, see text.

Xenon-ion implantation into the polished sample (350 kV, 5×10^{15} ions/cm^2) produces a conductivity equal to that of the rough surface above ~0.3 K. In other words, the specular reflection seen between 0.3 and 2 K on the unirradiated sample has been eliminated by this treatment. At lower temperatures, however, the specular reflection is less affected. This observation answers the first question asked in the introduction: Diffuse phonon scattering can also be caused by disordering a relatively thin layer near the crystal surface. A damage of the surface itself is not required.

One may assume that the disorder caused by the ion implantation will scatter the phonons, as is known in disordered solids. Consider the phonon mean free path in a fully amorphous solidlike silica. In this glass, the average phonon mean free path at 2 K is 3.10^4 Å,[18] and at 0.3 K it is 4.10^5 Å. Both of these lengths are approximately 100 times larger than the wavelengths of the phonons carrying the bulk of the heat at the two temperatures. Under the conditions of ion implantation in the present experiment (Xe$^+$, 350 kV), all ions are stopped in a layer no thicker than ~500 Å with the peak of the damage occurring at ~400 Å. Since all phonons seem to be diffusely scattered in this very thin layer (for $T > 0.3$ K), their mean free path must be of the order of its thickness, 500 Å. It follows that the damaged thin layer is a far more effective scatterer for the phonons than is the bulk of an amorphous solid, which is known to be a very effective scatter. Another puzzle is the low-temperature cutoff of the diffuse scattering.

We also explored the effect of a thin metal film deposited on the polished (and unirradiated) sapphire crystal. Figure 2 shows the remarkable result that a gold film of approximately 50 Å in thickness produces diffuse scattering which is almost identical to that resulting from ion implantation. (The sequence of the thermal-conductivity measurements was, of course, different: First, the sample with the clean, polished surface was measured, then the sample with a thin gold film. Next, the sample was measured after ion implantation, with the gold film removed prior to the measurement. Finally, the abraded, milky-looking sample was measured.) The diffuse scattering by the thin gold film shows clearly that the phonons travel all the way to the surface of the sapphire crystal, and are scattered by the metal film which is so weakly attached that it can be wiped off with the fingers. Even more mysterious, however, is the observation that the low-temperature cutoff for the diffuse scattering is almost identical to that observed on the ion-implanted sample. This observation suggests that the mechanism by which the phonons are scattered is similar in both cases. It is, however, very difficult to see a physical resemblance between the two scatterers. A gold film 50 Å in thickness on the sapphire is likely to be discontinuous, consisting of a patchwork of metal droplets. This assumption is based on the observation by von Bassewitz[19] that gold films evaporated onto polished quartz substrates at room temperatures have larger electrical resistances than expected from their thickness determined by optical means, if the films are less than 120 Å thick (see, in particular Fig. 6 of Ref. 19). For Bi_2O_3 and SiO the critical thicknesses are 70 and 50 Å, respectively. In contrast to these weakly bonded droplets, the thin layer damaged by the ion implantation is thought to be a strong, continuous, uniform layer. It is difficult to see a similarity in the degrees of freedom which might couple to the phonons in both cases.

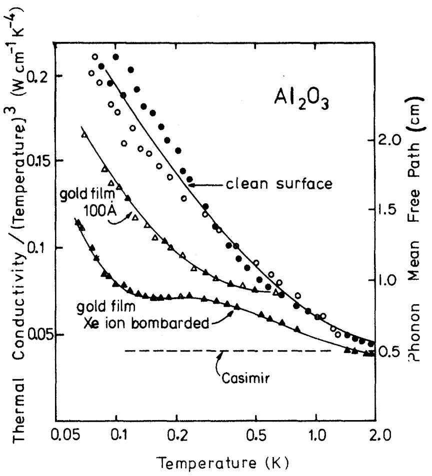

FIG. 3. ΛT^{-3} for a second Al_2O_3 single crystal. Open circles represent ΛT^{-3} for a polished surface; open triangles for a Au film, 100-Å thick. Closed triangles for same gold film, but after Xe ion bombardment which resulted in a thinning of the gold film through sputtering. Closed circles denote ΛT^{-3} after removal of gold film remnants, when thermal conductivity has recovered. Prior to the first measurement, the sample had not been cleaned. Thus, accidental surface contamination might explain why the conductivity measured during the last run (closed circles) is actually somewhat higher below 0.2 K.

In another set of experiments, we explored the effect of the thickness of the gold film. A 100-Å-thick gold film was also found to cause diffuse scattering (see Fig. 3). The effect, however, was much less than that observed with the thinner film (Fig. 2). Xenon ion bombardment of the sample covered with this thicker gold film (80 kV, 5×10^{14} ions/cm^2) resulted in a thinning of the film (probably by sputtering), as could be told by the change in its color (from green to a blue-gray or violet). This treatment caused an increase in diffuse phonon scattering (see Fig. 3). Subsequent removal of the damaged gold film restored the conductivity to that of the polished sample. Based on the estimated penetration depth of the 80-kV xenon ions in the gold film (~ 100 Å),[8] we estimate that very few ions reached the sapphire in this experiment. Thus, the radiation damage was confined largely to the gold film.

A comparison of the increase in diffuse phonon scattering in our experiments is shown in Fig. 4. Writing the thermal conductivity Λ as

$$\Lambda = (\tfrac{1}{3})C_v v l \,, \tag{1}$$

where C_v is the measured specific heat, v the Debye speed of sound calculated from C_v, and l the average phonon mean free path (see the caption of Fig. 1), we determined the additional phonon scattering with the expression

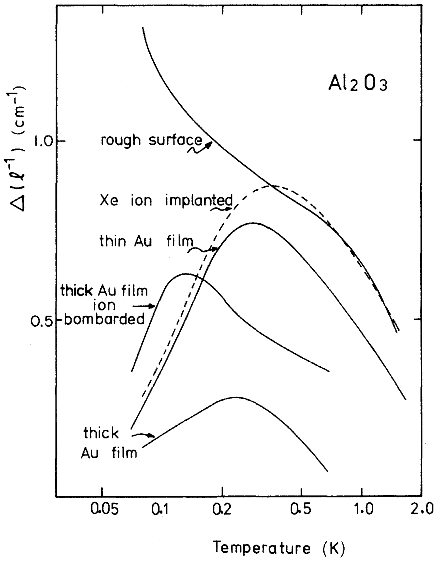

FIG. 4. Additional phonon scattering $\Delta(1/l)$ [Eq. (2)] caused by surface treatments. "Thick" Au film means 100 Å, "thin" means 50 Å in average thickness.

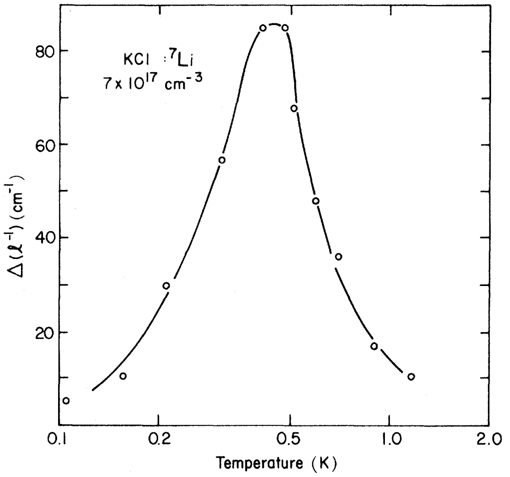

FIG. 5. Scattering strength $\Delta(l^{-1})$ as defined in Eq. (2) for strongly scattering bulk defects. The Li$^+$ ion performs a tunneling motion in the K$^+$ vacancy it occupies. Defect concentration 7×10^{17} cm^{-3} (44 ppm). The average resonant frequency associated with this scattering is $f_0=3.6\times10^{10}$ sec^{-1}, 1.2 cm^{-1} in the wave-number measure (see Ref. 21).

$$\Delta(l^{-1})=l_{\text{expt}}^{-1}-l_{\text{clean}}^{-1}\;, \tag{2}$$

where "l_{clean}" refers to the mean free path for the polished and untreated sapphire.

The largest increase in diffuse phonon scattering results, obviously, from roughening the surface [top curve in Fig. 4; the fact that $\Delta(l^{-1})$ does not saturate at $1/l_{\text{Casimir}}$ at low temperatures results from the fact that A drops faster than T^3 below 0.2 K in the roughened sample, as shown in Fig. 2]. The thick (100 Å) gold film causes a small increase in diffuse scattering, which appears to peak near 0.3 K. Ion bombardment enhances the diffuse scattering. Again, the effect appears to peak, although at a somewhat lower temperature. The thin evaporated film, and the Xe$^+$ ion-implanted layer on the sapphire crystal, cause yet a larger effect on the thermal conductivity. Above 0.3 K, they both induce as much diffuse scattering as complete roughening of the surface does.

This comparison has brought out one new aspect not evident in the data presented in Figs. 2 and 3: The enhancement of the diffuse scattering caused by the surface treatment appears to peak at some temperature, which indicates resonance scattering. The experimental evidence, however, is somewhat uncertain at this point, since the difference between the conductivities of the polished and the abraded samples also drops to zero near the upper end of the temperature range covered. Consequently, the quantity $\Delta(l^{-1})$ as defined in Eq. (2) must also decrease at these temperatures. The question whether $\Delta(1/l)$ drops faster than expected on the basis of the shrinking "window" between the polished and roughened sample alone cannot be answered at this time except possibly for the ion-implanted, sputtered, initially 100-Å-thick gold film, which shows the decrease of the additional scattering strength even in the raw data quite clearly (see the dip around 0.15 K in Fig. 3). For the same gold film prior to implantation, the experimental accuracy is not adequate to draw a firm conclusion (see Fig. 3). Consequently, resonant scattering for our surface treated samples must remain an open question at this point. Nevertheless, a comparison with the resonant scattering observed on defects in the interior of crystals will help again to visualize the impressive strength of the scattering in the surface treated crystals.

Tunneling impurities are among the strongest phonon scatterers known in the interior of dielectric solids at low temperatures.[20] Figure 5 shows the resonance scattering produced by Li$^+$ ions tunneling in K$^+$ vacancies in KCl, as observed in thermal conductivity.[21] For a concentration of 7×10^{17} cm^{-3} (44 ppm) of Li$^+$ ions, the phonon inverse mean free path as defined in Eq. (2) peaks at $\Delta(l^{-1})=80$ cm^{-1} (at $T=0.44$ K). This is over 2 orders of magnitude larger than the peak value observed, for example, on the sapphire with the 100 Å, ion-bombarded gold film, which is 0.6

cm^{-1}. [$\Delta(l^{-1}(T))$ has also a larger width than the Li^+ resonance curve, suggesting possibly a range of resonance frequencies in the gold film; we shall ignore this here.] The enormous strength of the scattering by the gold film becomes apparent if one compares the small volume to which it is confined, which is 8×10^{-6} of the entire cross section ($=0.5\pi\times10^{-6}\ \text{cm}^2/0.25^2\pi\ \text{cm}^2$). This means that $\Delta(l^{-1})$ in the gold film itself is $(0.6\ \text{cm}^{-1}/80\ \text{cm}^{-1})/8.10^{-6}\approx10^3$ larger than in the doped KCl shown in Fig. 5, assuming the scattering occurs uniformly throughout the gold film.

An enhancement of the diffuse scattering of electrons at crystal surfaces has previously been observed in measurements of the electrical resistance of well-annealed metal films. Their resistance was found to increase after a second, thin metal film had been deposited on its surface.[19,22] The diffuse scattering increased when the second film had been deposited at low temperatures through rapid quenching from the vapor phase. The interpretation given was that the electrons in the substrate film were diffusely scattered upon striking the surface covered by the disordered crystallites of the second film.

Since the phonon scattering by the gold film diminishes with increasing thickness, it would be tempting to consider individual drops of the discontinuous gold film as potential scatterers. They might conceivably oscillate on the surface, thus causing resonant scattering with low resonant frequencies, because of their large mass and weak binding force. With increasing thickness, the film becomes more continuous,[19] and this might explain the decrease of the scattering. One way to test this model would be to study more tightly adhering metal films, or metal films of known, different structures. Such measurements are underway. It is, however, very difficult to extend this model to the ion-implanted sapphire layer, which is believed to be continuous and strongly bound to the rest of the crystal. For this radiation-damaged layer the picture of atomic scattering centers would be more likely, but here the strength of the scattering presents problems, as we saw previously. Strong anharmonicities in the irradiated, and hence, strained crystal lattice might constitute an attractive, although admittedly hazy picture. But where are the anharmonic forces in the gold-covered crystal, since the gold is so weakly bonded that it barely sticks to the surface? The fact that the two entirely different surface treatments lead to such similar results is the most puzzling and fascinating observation in this work.

IV. CONCLUSION

Besides the well-known surface roughening, various irregularities on or close to polished crystal surfaces can also cause diffuse phonon scattering. Its magnitude greatly exceeds that previously observed for scattering centers in the bulk of dielectric crystals. The nature of these surface scattering centers is unknown at this point. Because of their potential importance for heat transport across interfaces between solids, as well as for thermal equilibration of surface layers applied to bulk solids, a better understanding of these centers presents a challenging task.

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