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Thermal transport in deformed lithium fluoride

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The thermal conductivities κ of LiF crystals, deformed by compression, have been measured over the temperature range 0.05 – 5 K. Below ~2 K a fraction of the thermal phonons are scattered strongly by defects while another fraction is only weakly scattered and can propagate distances of ~1 cm even in heavily deformed LiF. The fact that the strong scattering can be suppressed by modest γ irradiation suggests that the active defects are fluttering dislocations. At $T \gtrsim 2$ K essentially all phonons are scattered by defects. Above 2 K the reduction in κ with deformation depends on the density of defects or impurities previously present in the sample. Available evidence suggests that isolated dislocations are not responsible for the strong phonon scattering at $T \gtrsim 2$ K.

I. INTRODUCTION

Early measurements on deformed dielectric crystals demonstrated[1–4] that deformation greatly reduced the thermal conductivity at temperatures below ~25 K. It was assumed that the phonon scattering was caused by dislocations introduced into the crystal during deformation but the measured scattering strength was found to be a factor of 100 – 1000 larger than calculated for sessile dislocations.[5] A much stronger scattering strength was predicted[6,7] if the dislocations could "flutter" like an elastic string. The dislocation could then absorb a phonon and reradiate the energy as another phonon in a different direction. The dislocations are assumed to be pinned at a statistical distribution of pinning points with a mean separation $\bar{L}$ between pinning points. Support for this model was obtained from thermal conductivity and ballistic-phonon measurements[8,9] on deformed samples of LiF which had been γ irradiated to introduce additional pinning points and hence reduce $\bar{L}$.

In LiF deformed by shear or bending, it has been observed that only a fraction of the phonons are scattered by defects.[8,9] The remaining fraction is scattered by the surfaces of the samples just as in undeformed crystals. Thus the total thermal conductivity κ may be written

$$\kappa = \kappa_B + \kappa_D , \tag{1}$$

where κ_B is the conductivity contributed by the fraction of phonons scattered by surfaces and κ_D is that contributed by phonons scattered by defects. Following deformation $\kappa \simeq \kappa_B$, and κ_D is essentially unavailable.[8,9] Since the magnitude and other details of the phonon-defect interactions are contained in κ_D, this information is also unavailable. The sole effect of additional deformation is to further decrease κ_D and thus κ is essentially independent of the amount of deformation or the number of dislocations present.

One qualitative result obtained from the thermal conductivity measurements was that the reduction in thermal conductivity by deformation occurred over too broad a range in temperature to be explained by fluttering dislocations.[9–11] This has led to the suggestion[10,11] that the defects which dominate phonon scattering are dislocation dipoles rather than individual isolated dislocations. It is argued that dipoles in LiF greatly outnumber isolated dislocations and that, in etch-pit counts, only the density of isolated dislocations is measured. Assuming that dipoles outnumbered isolated dislocations by a factor of ~30 permitted theory and experiment to be reconciled.

In an attempt to obtain more detailed information on the phonon-dislocation interaction we undertook the present work on LiF crystals deformed by compression. Earlier data[1,12,13] obtained at $T \gtrsim 2$ K (Fig. 1) indicated that the thermal conductivity of compressed samples decreased with the amount of deformation. In brief, *all* phonons were being scattered by defects introduced by deformation. The term κ_B in Eq. (1) being negligible

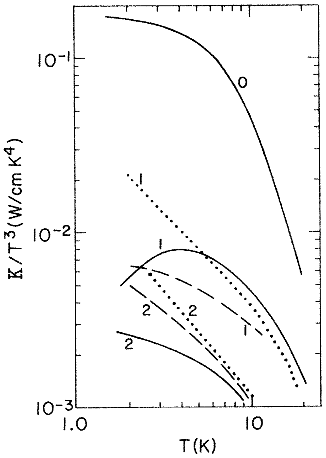

FIG. 1. Thermal conductivity of LiF, divided by T^3 to allow the vertical scale to be expanded. Solid lines from Ref. 12: 0, 0% deformation; 1, 6.2% (1.3×10^8 etch pits cm^{-2}); 2, 13.3% (3.5×10^8 cm^{-2}). Dotted lines from Ref. 1: 1, 2.4% (1.8×10^7 cm^{-2}); 2, 4.0% (4.6×10^7 cm^{-2}). Dashed lines from Ref. 13: 1, 5.2% ($\approx4\times10^7$ cm^{-2}); 2, 10.3% ($\approx10^8$ cm^{-2}). All measurements were on different samples; all deformation was by compression.

would not mask the scattering information contained in κ_D. We therefore hoped to investigate in detail the mechanism of phonon scattering by fluttering dislocations, again using γ irradiation to manipulate the dislocations. In previous work,[8,9] γ irradiation had been most effective at $T \lesssim 2$ K, and thus we extended the present measurements to $T \lesssim 0.1$ K.

II. EXPERIMENTAL PROCEDURE

Harshaw LiF crystals of ~5 cm length were cut with surfaces on (100) planes. The samples were deformed at room temperature by compression along the long axis, the lateral dimensions following deformation are given in Table I. During deformation, the sides of the samples were supported by brass blocks, and the ends were covered with indium sheets.

A typical plot of load versus deformation is shown by the dotted line in Fig. 2. The yield stress of ≈ 0.15 kg/mm^2 is lower than the ~0.4 kg/mm^2 observed by previous workers who had measured the thermal conductivity.[1,12] Assuming the higher yield stresses may have resulted from less pure[14] or less perfect[15] samples and wanting to reproduce the behavior in κ observed by others, we submitted sample G (Ref. 16) to 50 000 rads of γ irradiation prior to deformation. The load versus deformation plot of sample G is shown by the solid line in Fig. 2. The γ irradiation did increase the yield stress to ~0.45 kg/mm^2.

We did not make etch-pit counts on these samples. Prior work on LiF deformed by compression[1,12,13,17] indicated that the etch-pit count was roughly proportional to the deformation $\Delta l/l$, reaching $\sim 2\times10^8$ cm^{-2} at $\Delta l/l \approx 10\%$.

Thermal conductivity data were obtained by using two Matsushita carbon thermometers[18] to measure a temperature gradient established by an electrical heater. Thermal contact between refrigerator and each crystal was provided by thin copper foil using GE7031 varnish as a thermal bonding agent.

TABLE I. Dimensions, deformation, and γ-ray exposure of LiF samples. Samples G, H, and J had not been irradiated by the vendor, although A and B may have been irradiated. We exposed sample G to γ irradiation prior to deformation.

Sample	Dimensions (cm^2)	Deformation (%)	γ irradiation (10^3 rads)
A	0.61×0.64	4.5	0
B	0.58×0.70	9.0	0
B1	0.58×0.70	9.0	5
B2	0.58×0.70	9.0	55
B3	0.58×0.70	9.0	555
G	0.59×0.67	10.0	50 (prior)
H	0.67×0.69	10.0	0
J	0.70×0.77	10.0	0
J_1	0.30×0.38	10.0	0
J_2	0.32×0.36	10.0	0

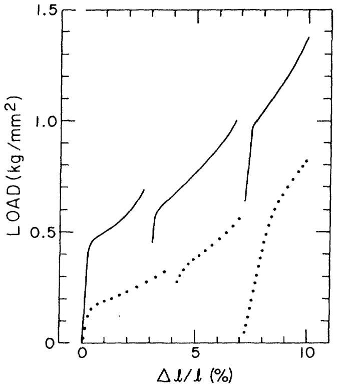

FIG. 2. Load versus compression for two LiF samples. Near deformations of $\Delta l/l \approx 3\%$ and $\approx 7\%$, the Instron was reset. Dotted line, sample *H* which was similar to sample *J* of Table I. Samples *A* and *B* had $\sim 50\%$ larger shear stresses than sample *H*. Solid line, sample *G* which had been exposed to a γ irradiation of 50 000 rads. (1 kg/mm^2 $\simeq 10^7$ Pa.)

The end of the crystal was clamped mechanically to avoid vibrational heating. The carbon thermometers were calibrated *in situ* against one or more germanium resistance thermometers. The germanium thermometers had been calibrated on the EPT 76 temperature scale against a set of superconducting fixed points[19] using a magnetic thermometer[20] for interpolation.

The surfaces of the samples *A*, *B*, and *G* were not abraded, while sample *J* (as well as J_1 and J_2) was abraded with air-borne powder. Abrasion ensures that most of the phonons which strike a surface are scattered "diffusively," producing a phonon mean free path limited by the size of the sample. This maximum mean free path is nearly frequency and temperature independent. As samples *A*, *B*, and *G* were to be used in specific-heat measurements,[16] we wished to avoid the lattice defects created by abrasion.

III. RESULTS AND DISCUSSION

The thermal conductivity κ of sample *B*, deformed in compression by 9% is shown by the circles in Fig. 3. The thermal conductivity of the sample *B*, had only boundary scattering been present, would be represented (roughly) by the top margin of the figure. For unabraded, undeformed samples the thermal conductivity rises well above this magnitude due to specular scattering of phonons from surfaces.[9] The maximum in κ vs T for this and the other samples lies at $T \gtrsim 10$ K.

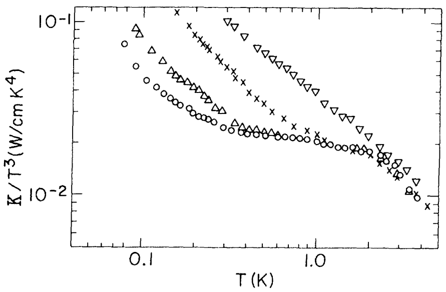

FIG. 3. Thermal conductivity divided by T^3 for LiF sample *B*. ○, deformed 9% by compression; Δ, deformed sample after γ-ray exposure of 5000 rads; ×, after additional exposure of 50 000 rads; ∇, after additional exposure of 500 000 rads.

The effect of subsequent exposure of sample *B* to γ irradiation[21] is also shown in Fig. 3. The κ at low temperature is restored toward its predeformation magnitude just as in sheared or bent samples.[8,9] A simple qualitative explanation is that the phonons are scattered by dislocations (or by dislocation dipoles), and that γ irradiation provides additional pinning points for the dislocations. This decreases $\bar{L}$, raising the resonant frequencies of the dislocations. Thus low-frequency phonons are not scattered and the κ at low temperatures, which is provided by low-frequency phonons, is increased. In brief, the effect of γ-ray pinning suggests that phonons can be scattered strongly by fluttering dislocations (or dipoles) in LiF crystals deformed by shear, by bending or by compression.

At temperatures above ~ 2 K, the data of Fig. 3 are considerably larger in magnitude than found in previous measurements made on samples deformed by $\Delta l/l \gtrsim 5\%$. This was also true for other samples, as shown for example in Fig. 4 for sample *A*. In addition in Fig. 4 we see by comparing samples *A* and *B* only a weak dependence of κ on strain. We thought these differences between the behavior of our samples and those of previous workers might be related to the larger shear stress of their samples. As an extreme example, the data of Ref. 1, the dotted curves of Fig. 1, represents the greatest reduction in κ for a given deformation. The samples of Ref. 1 had to be heated to $\sim 180\,^{\circ}$C during deformation to avoid cracking; they could not be compressed at room temperature. We therefore hardened sample *G* by exposure to 50 000 rads of γ irradiation prior to deformation. This in-

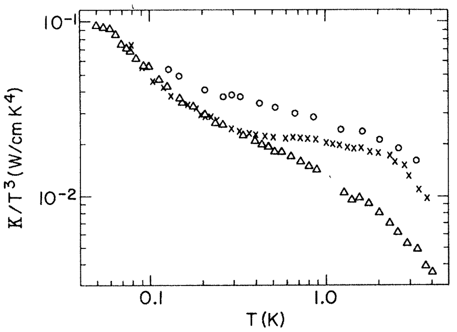

FIG. 4. Thermal conductivity divided by T^3 of deformed LiF samples. ○, sample *A*, 4.5% deformation; ×, sample *B*, 9% deformation; Δ, sample *G*, exposed to 50 000 rads of γ irradiation, then deformed by 10%. The top margin of this figure, as for Fig. 3, represents roughly κ/T^3 if phonons were scattered only by the surfaces of the samples.

creased the shear stress by a factor of ~ 2 relative to sample *B* (Fig. 2) and further reduced κ for 10% $\Delta l/l$ at $T > 2$ K by a factor of 2.5 (Fig. 4). The thermal conductivity data now more closely resemble the data of Ref. 1 (Fig. 1). Thus, the hardness of the crystal (i.e., the quantity of defects or impurities present in the crystal prior to deformation) has a significant influence over the resulting reduction in κ at $T \gtrsim 1$ K.

There is additional evidence (Fig. 1) of the effect of crystal hardness on the thermal conductivity of compressed crystals at temperatures above ~ 2 K. Compression decreases the thermal conductivity. However, the reduction in κ is not simply proportional to the amount of compression $\Delta l/l$. In fact κ is reduced by a factor greater than the increase in $\Delta l/l$ (e.g., a factor of ~ 4 reduction in κ versus a factor of ~ 2 increase in $\Delta l/l$ at higher temperatures). Therefore, the deformation of a sample enhances the effect on κ of subsequent deformation. This is undoubtedly related to strain hardening.[17]

Evidence at hand suggests that the reduction in κ at $T \gtrsim 1$ K is *not* due to isolated dislocations. In Fig. 1, the etch-pit counts (and hence the density of isolated dislocations) for the samples represented by the dotted lines were a factor of ~ 10 smaller than those of the samples represented by the solid lines, yet κ is roughly the same at higher temperatures. Since the dotted lines were obtained from a much harder crystal, we might conclude that it is the "debris"[22] produced during plastic deformation which strongly scatters phonons. Experimental evidence from NaCl argues against vacancies as a potential candidate.[3]

The fluttering of dislocation dipoles might account for the scattering but the distribution of the dipole dislocation-dislocation separation distances *d* assumed in Refs. 10 and 11 predicts $\kappa \propto T^n$, $n > 3$. This does not account for the $\kappa \approx T^2$ temperature dependences of Fig. 4. The $\sim T^2$ dependence at $T \gtrsim 2$ K could be explained by scattering from the strain fields of sessile dislocations in dipoles when the phonon wavelength λ is much less than *d*. (For larger λ, the scattering of a dipole is reduced below that of a single dislocation.[23,24]) At $T = 2$ K, $\bar{\lambda} \approx 200$ Å. The number of dislocations required[25] having $d > 200$ Å would be $\sim 5 \times 10^{10}$ cm^{-2} for sample *G*. We do not know if sample *G* could contain a density of dipoles a factor of ~ 100 larger than the density of isolated dislocations deduced from the deformation. It should be kept in mind that these would be sessile dipoles, as specific heat measurements[16] limit the number of fluttering dipoles in sample *G* to less than $\sim 10^9$ cm^{-2}.

Our discussion now returns to the temperature region below 1 K. We noted that κ was only weakly dependent on deformation for several samples and that κ/T^3 had a weak temperature dependence between, roughly, 0.2 and 2 K. We were curious to know if this behavior was caused by some fraction of the phonons being scattered by the surfaces of the samples as in sheared[8] or bent[9] samples. We therefore abraded the surfaces of sample *J* to reduce specular scattering. The thermal conductivity data are shown in Fig. 5. The temperature dependence κ is close to T^3 from 0.2 to 1.5 K. We then cut sample *J* into samples J_1 and J_2 in which the lateral dimensions were reduced by a

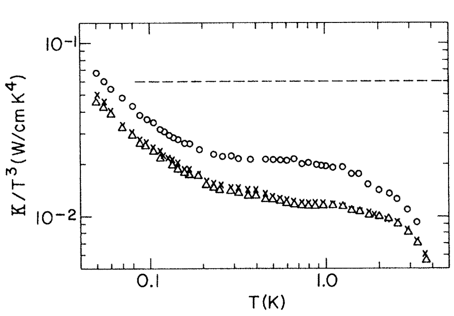

FIG. 5. Thermal conductivity divided by T^3 of LiF samples after deformation by 10%. ○, sample *J*; ×, sample J_1; Δ, sample J_2. Samples J_1 and J_2 were cut from sample *J* and have lateral dimensions $\sim \frac{1}{2}$ of sample *J*. The top margin represents, roughly, κ/T^3 of sample *J* if phonons were scattered only by sample surfaces. The dashed line provides the same information for samples J_1 and J_2.

factor of 2 (see Table I). Indeed the κ was reduced by a factor of ~ 2 (see Fig. 5). This provides evidence that some fraction of the phonons can propagate through ~ 1 cm of heavily deformed LiF without being scattered by defects. It also means that Eq. (1) may apply to compressed samples as well as to sheared and bent samples and that the desired phonon-scattering information contained in the term κ_D is masked by κ_B. The boundary scattering experienced by a *fraction* of the phonons also explains (i) the dependence of κ on the size of compressionally deformed samples noted previously in the literature,[26] and (ii) the approach of κ to a T^3 temperature dependence previously observed[3,26,27] as T was reduced toward 1 K.

The lateral dimensions of sample J were decreased by a factor of two but the corresponding reduction in κ/T^3 (e.g., near 0.8 K in Fig. 5) was only a factor of 1.7. This difference appears to be real and may indicate that the term κ_D in Eq. (1) is finite at $\kappa_D/T^3 \approx 3.6\times10^{-3}$ W/cm K^4. There is also the possibility that the apparent boundary scattering mean free path responsible for the term κ_B may depend on bulk scattering processes.[28] In addition, phonon focusing and other phenomena[10,11] must be considered in any attempt to explain these data.

IV. SUMMARY

At $T \lesssim 2$ K in LiF crystals deformed by compression a fraction of the thermal phonons are scattered by defects. Another fraction is only weakly scattered and can propagate distances of ~ 1 cm even in heavily deformed LiF. This second fraction dominates the thermal conductivity of deformed samples, obscuring the desired information on phonon-defect interaction. Exposure to a modest γ irradiation suppresses the defect scattering, suggesting that the active defects are fluttering dislocations or dislocation dipoles.

At $T \gtrsim 2$ K, essentially all phonons are scattered by defects. The reduction in thermal conductivity with deformation depends on the density of defects (or impurities) already present in the sample. Available evidence, which is meager, suggests that isolated dislocations are not responsible for the phonon scattering. Dislocation dipoles may be invoked but will likely require an *ad hoc* selection of adjustable parameters to explain the temperature dependence of the thermal conductivity.

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