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# Strengthened lithium for x-ray blast windows

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Lithium's high x-ray transparency makes it an attractive material for windows intended to protect soft x-ray diagnostics in high energy density experiments. Pure lithium is soft and weak, but lithium mixed with lithium hydride powder becomes harder and stronger, in principle without any additional x-ray absorption. A comparison with the standard material for x-ray windows, beryllium, suggests that lithium or lithium strengthened by lithium hydride may well be an excellent option for such windows. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2937203]

## I. INTRODUCTION

Beryllium is uniquely suitable for use with soft x-rays because it combines excellent mechanical strength with good x-ray transmission. This paper suggests that other materials, notably lithium and some of its variants, could work equally well if not better than beryllium for blast shields. These nonstandard x-ray windows protect soft x-ray diagnostics in high energy density experiments.[1] The high x-ray fluence in such experiments sometimes evaporates the shield's front face, and it may tear too due to the blast that usually follows the x-ray pulse. The result is beryllium dust or scrap. Both are considered severe health hazards that may cause major problems for the experimenter and delay the experiment.

The relevant soft x-rays have typical photon energies of a few keV and fluences up to a $\mathrm{MJ/m^2}$. The x-ray source is usually a small amount of solid or gas with peak temperature $T$ on the order of $T \simeq 1$ keV ($\simeq 10^7$ K), rapidly heated by an intense laser or a powerful electrical discharge and rapidly cooled by the x-rays themselves. Ultrafast lasers can use minute amounts of material and do not need much energy to achieve a multi-keV temperature. However, slower lasers or pulsed power equipment[2] is generally needed to emit up to megajoules in x-ray energy from a larger-mass source. If it were a blackbody, a tiny ball with $T \simeq 1$ keV and radius $r = 100\ \mu$m radiates most intensely around a photon energy $h\nu \simeq 3T \simeq 3$ keV, with a total power $P = 4\pi r^2 \sigma_{\mathrm{SB}} T^4 \simeq 1$ TW. Here, $\sigma_{\mathrm{SB}} \simeq 6 \times 10^{-8}\ \mathrm{W/m^2\,K^4}$ is the Stephan–Boltzmann constant. How closely a hot ball of material approximates a blackbody depends on many variables including the material's mass and its atomic number. X-ray cooling of source material slows down rapidly (as $T^4$) with temperature $T$. Hence, once the x-ray pulse is over the source material is still hot enough, and the pressure high enough, that it explodes. The explosion is kept away from the soft x-ray diagnostics by the blast shield.

The blast shield must obviously be transparent enough for the soft x-rays of interest, but still strong enough to withstand the blast. For the harder x-rays, with photon energies $h\nu \sim 100$ keV, say, this is not usually a problem: hard x-rays go through most materials, so that a blast shield for hard x-rays can be thick (tens of millimeters) and the material choices are legion. In contrast, soft x-rays already stop in thin (micronlike) layers of all strong materials (except beryllium), and a micron-thick window is necessarily weak. Only a window from beryllium can be reasonably thick: 100 $\mu$m beryllium passes 1/4 of the x-rays at $h\nu = 2$ keV and 0.85 of 4 keV x-rays, while just over 1% and less than half of these x-rays would pass through the same thickness of carbon (fibers, say). Both beryllium and carbon are strong, and Be is the standard with which other window materials are measured.

One way to quantify the x-ray transmission $T = T(h\nu) = \exp(-d/\ell)$ is with the penetration length, $\ell = \ell(h\nu)$, the thickness $d$ of a foil that passes a fraction $1/e \simeq 0.37$ of the x-rays. An alternate measure is the mass attenuation coefficient $(\mu/\rho)$, the inverse of the mass per unit area for $T = \exp(-1)$. Since the mass per unit area is proportional to the number of electrons per unit area, and since x-rays interact primarily with electrons, $(\mu/\rho)$ is similar for all materials. The soft x-rays at issue here are generally in the photoelectric regime: the mass attenuation coefficient then varies with photon energy $h\nu$ as $(\mu/\rho) \sim (1/h\nu)^3$, and with atomic number $Z$ approximately as $(\mu/\rho) \sim Z^3$. A promising material for use with soft x-rays besides beryllium, with $Z = 4$, is lithium, with $Z = 3$.

Indeed, lithium is a good material for an x-ray refractive lens.[3–5] Magnetic focusing lenses for high energy protons[6] also use lithium: it minimizes charged particle scattering (per unit stopping distance) because of its low nuclear charge. This paper shows that lithium can also be a viable material for blast windows for soft x-rays, even when mechanical strength is important.

Lithium has a clear advantage over beryllium when strength is not important. This is true for a sacrificial filter. Sometimes, the only purpose of such a filter is to take out undesirable, too-soft x-rays, e.g., when the desired measurement can be completed before any material from the x-ray source could get to the diagnostic. The x-rays could then be strong enough to evaporate part or all of the window (but not

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so strong that the radiation ionizes the filter fully, lest the material might no longer filter soft x-rays well enough). The filter is blown back by any material that evaporates off its surface, and by the exploding x-ray source. For a given impulse on the filter material, the speed is lowest when the filter's mass per unit area is maximum. For a given x-ray transmission, this is the material with the highest mass attenuation coefficient $\mu/\rho$ itself. Mechanical strength is not important for such filters.

Judged from the mass attenuation coefficient alone, cryogenically cooled solid deuterium would be the best material for such a sacrificial filter. Unfortunately, $\sim$4 K solid deuterium is difficult to make,[7] so that an x-ray filter from solid deuterium is justified only in extreme circumstances, when the x-rays are so powerful that they would convert any filter material, including lithium, into an ideal gas. Therefore, in most cases, lithium is the best material for a sacrificial filter.

This paper deals with a second type of nonstandard x-ray window: the x-rays do not evaporate the window, but the window must be strong enough to survive the blast. A complete analysis of this situation depends on the experiment's specifics. The x-rays could, for example, be strong enough to evaporate only a small part of the window's front face, while the window's back side barely heats up (and the material in between shows a gradient in temperature). Material evaporation could be so sudden and strong that a shock wave travels from the window's front to its back, where this could cause spall, just right for the window material to acquire some constant backward momentum density over its surface, or so slow that the window can even move during the x-ray pulse. Moreover, the pressure pulse that follows the x-rays could be smaller than the one from x-ray ablation, or swamp it.

The window's response is just as complicated: does it break loose from its support, or is the window strong enough to survive both x-ray irradiation and the pressure pulse? In addition, what is the window's final state: is it reusable because the stresses remained in the elastic regime, or has it deformed inelastically so that it must be disposed of? This paper ignores any such complexity and treats the soft x-ray window as if it were under stationary pressure. While this (over)simplification may not fit any particular soft x-ray experiment, it allows an analytical comparison between the various materials for soft x-ray windows, Be, Li, and its variants.

For a given geometry, the maximum static pressure on a thin foil without bending stresses, a membrane, is in large part determined by the material's ultimate tensile strength $\sigma_{\mathrm{UTS}}$. However, when the membrane is made from a plastic material such as lithium that can stretch substantially, like taffy, the maximum strain $\epsilon_{\max}$ and even the geometry that the membrane evolves into could become relevant. These three cases give three different figures of merit for soft x-ray window materials.

Beryllium seems ideal for survivable x-ray windows under static loading, but it has two problems: health and (for disposable windows) cost. Lithium is not expensive and it has no known health problems, but it comes with its own challenges. One is chemical: lithium corrodes rapidly in typical laboratory air. X-ray refractive lenses made from lithium are therefore packaged in atmospheric pressure helium or under vacuum, in a hermetically closed container with beryllium windows to let the x-rays in and out. Lithium's corrosion in air is not a problem in a soft x-ray experiment itself, because the soft x-rays need a good vacuum too: air's approximate atomic number $Z \simeq 7$ is too high for good transmission of the soft x-rays. Bringing the lithium safely into the experimental chamber, from the glovebox in which the material is made and packaged under dry helium or dry argon, will need the appropriate equipment and care.

This paper shows that well-known techniques[8] such as alloying, work hardening, and dispersion strengthening indeed make lithium substantially stronger than pure lithium. Lithium's bcc crystal structure should make its strengthening properties similar to those of other metals with the same crystal structure. Indeed, like bcc copper, lithium shows substantial work hardening that was characterized only recently.[6] At room temperature, lithium's ultimate tensile strength $\sigma_{\mathrm{UTS}} \simeq 1$ MPa, increasing more than tenfold under cryogenic cooling[9] (to 77 K). Unfortunately, work-hardened and heat treated lithium is inconvenient in x-ray windows, because a bcc metal must be maintained (far) below $2/3$ of the melting temperature $T_m$ ($\simeq$454 K for lithium) to forestall annealing. Since for lithium $2/3T_m \simeq 300$ K, just about room temperature, work-hardened Li will fully anneal in room-temperature storage. In contrast, once the window is under the vacuum, it is easy strengthened further by cooling to 77 K.

Strengthening of weak metals by mixing in hard powders was demonstrated earlier for other weak metals,[10] notably for mercury[11] and lead.[12] The powder was iron. Mixing iron powder into lithium should also make lithium stronger, but with iron powder inside the mixture would no longer transmit the x-rays. However, all powders should have roughly the same mechanical effects, and there is a wide variety of powders to choose from. However, the powder must be made from atoms with the same or lower atomic number than lithium lest the x-ray transparency be affected. This leaves only one candidate, lithium hydride or LiH.

Lithium hydride transmits x-rays slightly better than lithium itself, and pure LiH has indeed been suggested as a good material for x-ray blast windows. However, LiH is an ionic crystal that is too hard and too brittle to manufacture into a thin foil as needed for soft x-rays (or into an x-ray lens[5]). Moreover, a thin window of brittle LiH would shatter when hit by a pressure pulse.

Contamination with highly x-ray absorbing atoms is always a problem in lithium's x-ray applications, and the same is true for LiH.[13] As is well known, the x-ray attenuation of mixtures is simply given by the x-ray properties of the components and their relative proportion. Since almost all atoms absorb x-rays much more than lithium and hydrogen, the mixture's x-ray transmission can be reduced by relatively few but highly absorbing impurities.

It is worth stating explicitly that the rule of mixtures does not apply to the strength of materials. In fact, a pure metal can become stronger by a suitable combination of mechanical work and thermal processing, without any additives.

Technical metals are almost always alloys. Usually, a small amount of the alloying material is enough to get the desired mechanical properties, which are achieved only when the alloy is then carefully heat and work treated. Likewise, dispersion strengthening depends not only on how many foreign particles are mixed in but also on the particles' size, shape, and orientation.

While some technically important alloys contain lithium as a minor constituent, solid lithium alloys with high x-ray transparency seem not to have been developed (but, there is a US patent[14] for a beryllium-lithium hydride foam). Pure lithium metal itself is well studied, often motivated by theoretical interests such as the relative ease of computing[15,16] lithium's properties. Lithium hydride is interesting theoretically for similar reasons.[16] Another reason for extensive work on lithium[17–20] is as a model system for a technologically important metal such as tungsten, which shares lithium's bcc crystal structure but is harder to deal with close to its melting point (for tungsten, $T_m \simeq 3683$ K). As function of the scaled (or homologous) temperature $T/T_m$, all bcc metals should be similar,[21,22] so that lithium at room temperature might mimic tungsten at 2430 K.

Carbon-based plastics are of course even easier in use than either beryllium or lithium, and much cheaper, but in many applications, the plastics (most with $Z \simeq 6$ or higher) absorb soft x-rays too much. Worse, at high enough fluence, the absorbed x-rays can melt the plastic, or make it so hot that it lost its strength when the pressure wave from the exploding x-ray source gets to the window shortly (microseconds) after the x-rays. All materials including beryllium and lithium lose strength when they become hot, especially when the temperature gets close to melting. However, lithium and beryllium heat up appreciably only under much higher fluences than needed to melt plastics.

As shown below, lithium metal indeed becomes substantially stronger by mixing it with LiH powder. In principle, the resulting material, Li–LiH, has an attractive combination of x-ray transparency and mechanical strength: it is on a par with beryllium, but without beryllium's health problems.

## II. PROCEDURES TO MAKE LI–LIH

Like aluminum, lithium exposed to air is immediately covered by a thin layer of lithium oxide that protects the metal from further oxidation. Unlike aluminum, lithium continues to oxidize when the air is humid. Lithium's oxide is hygroscopic, and the oxide dissolves in the water that the oxide extracts from the air. Lithium's oxidation is limited only when the air is dry enough, with a dew point below −50 °C or so, or in an glovebox free of oxygen. Besides oxygen and water, lithium at room temperature reacts slowly with nitrogen: absent a nitrogen purifier, the gas in a glovebox can be kept reasonably nitrogen-free by reacting the nitrogen away with hot lithium. The lowest-cost gas for gloveboxes, nitrogen, cannot be used in a glovebox intended for lithium (but $CO_2$ could, and may even be favored when LiH must be dealt with too).

The next-lowest-cost gas is argon. However, argon at atmospheric pressure attenuates soft x-rays (with energy $h\nu \geqslant 3.2$ keV above argon's $k$ edge) just as much as solid lithium metal. The helium atmosphere makes it easy to measure lithium's x-ray transmission, and to package lithium x-ray lenses.

In this work, the primary materials are battery-quality lithium metal (from Chemetall Foote, Kings Mountain, NC), and powdered LiH of 99.4% purity (from Alfa-Aesar). Although their catalog specifies this LiH to be a −8 mesh powder, with as largest particle $\simeq 2.4$ mm in size, the actual particles in the powder are very much smaller: estimating the sizes through a simple microscope suggests that most are smaller than about 5–10 $\mu$m. The powder could be made finer still by ball milling, and a uniform size distribution could be gotten by sieving the resulting LiH powder, but the available equipment needed for these operations was incompatible with the glovebox. Therefore, the LiH powder is used as received, without further processing.

It is easy to mix materials when both can be obtained as powders, or when both melt in the same temperature range. A powder with a high melting point may be difficult to mix with a soft metal. However, LiH powder turns out to mix easily into liquid lithium when this is hot enough.

One successful procedure is as follows. Heat lithium metal through its melting point, and remove the layer of contaminants from the molten lithium so that the liquid's surface is shiny. Pour LiH powder on top of the liquid. The powder does not mix with the lithium when the temperature is still below about 400 °C. However, as the lithium continues to heat, the LiH powder starts to mix into the liquid Li rather suddenly. Then, the heater can be turned off.

We speculate that mixing begins when the liquid lithium starts to wet the LiH powder, and that this occurs when the LiH becomes hot enough to dissociate.[23,24] Since the partial pressure of hydrogen in the glovebox is essentially zero, LiH dissociates much below the dissociation temperature at atmospheric pressure (680 °C). The decrease in liquid lithium's surface tension with temperature is too small to explain the wetting.

A particle of LiH dissociates first on its surface. Hydrogen escapes easily from the surface, while the hydrogen dissociates from a LiH molecule on the inside has a finite chance to rereact with the lithium it encounters as it diffuses on its way out. The particle's outside then tends to become a thin layer of liquid lithium, which would pull the remaining LiH particle into the bulk liquid through surface tension. This scenario, thermal dissociation on the surface followed by wetting and mixing, would make the LiH particles that are now dispersed throughout the liquid lithium smaller and smoother than the particles that make up the LiH powder from the bottle.

Whatever the reason(s), mixing hot enough liquid Li with LiH powder results in a slurry, with a consistency that varies with the relative amount of LiH. When the mixture is 50-50 (by weight) it resembles wet sand. Less LiH powder makes the mixture flow more easily, perhaps like pancake dough when only 10% or 20% LiH is mixed in. It has not yet been possible to measure the size, or better yet the size distribution, of the LiH particles after they are mixed in, and to quantify how much LiH is needed to get a mixture with specific flow properties.

One way to make x-ray windows from the material is from an extruded rod, by flattening it with a jeweler's mill. It was not possible to mix the material and to extrude a rod from a reusable vessel. To be reusable, the mixing vessel must remain almost vacuum tight through various heating cycles up to 400 °C, otherwise, liquid lithium (which wets the container's walls) seeps through the cracks during heating and mixing. It is therefore convenient to mix liquid Li and LiH powder in a disposable, seamless cup of stainless steel, and then to extrude the cooled-down mixture through a hole drilled in the cup's bottom. This method minimizes the corrosion of the warm Li–LiH material. When the glovebox atmosphere is good enough that the mixture does not corrode during cooling, it is easier to scrape the hot Li–LiH mixture out of the cup and let it cool on a sheet of stainless steel. The mixing cup can then be used again, which should limit contamination of Li–LiH by material dissolved out of the stainless steel. However, the material that remains on the wall affects the mixing ratio of the next batch. Other ways to make Li–LiH were not attempted, mostly for lack of the appropriate equipment.

Pure lithium is easily extruded as a rod through a $\simeq 2$ mm diameter hole, and even as a thin foil: in fact, lithium foil is produced commercially by extrusion. However, some samples of Li–LiH are so strong that up to 100 MPa pressure is needed to extrude it through a $\simeq 9$ mm hole. Foils thinner than about 1 mm are difficult to make from pure lithium by rolling: the thinner the foil, the more readily the lithium sticks to the rolling cylinders rather than remaining straight. In contrast, Li–LiH is strong enough to roll foils down to $\simeq 0.28$ mm even without lubricating the rollers. Thinner foils can be rolled out with more care, e.g., more frequent passes through the rolling mill at less fractional reduction per pass, and with lubricated rollers: good lubricants are chemically inert liquids such as anhydrous heptane or other alkanes. Heptane is convenient because it evaporates like water, hence, it stays on the rollers long enough to lubricate, but still evaporates fast enough to minimize any additional x-ray attenuation that could result if the lubricant were to embed itself in the Li–LiH foil.

Figure 1 is a $\simeq 0.28$ mm thick and $\simeq 60$ mm square sheet made by rolling out a 9 mm diameter rod. The material's density $\rho_{\text{Li–LiH}} \simeq 0.650\ \text{g/cm}^3$, a little heavier than pure lithium (with $\rho_{\text{Li}} \simeq 0.534\ \text{g/cm}^3$) but lighter than LiH ($\rho_{\text{LiH}} \simeq 0.78\ \text{g/cm}^3$), as expected.

## III. LI–LIH'S MECHANICAL STRENGTH

Hot isostatic pressing, infiltrating LiH powder with liquid lithium at elevated temperature possibly less than 400 °C might give densified Li–LiH directly, but the Li–LiH samples made by mixing have voids. These are easily eliminated by compressing the material, here, inside a 13 mm diameter stainless steel ring made from a standard 1/2–13 nut. This gives a Li–LiH cylinder that is thick enough, 11.3 mm, for a convenient measurement of the x-ray transmission. The same samples are also good for mechanical hardness testing. The data below are for a typical Li–LiH sample, with about 30% LiH. Samples with less LiH tend to be softer, those with more LiH harder: too much LiH (or insufficient mixing) can leave clumps of powdered LiH that form weak spots. A systematic study of strength as function of composition, particle size, and mixing quality awaits further work, which should include the exploration of alternative methods to make the material including hot isostatic pressing.

FIG. 1. (Color online) Square foil of 0.28 mm thick Li–LiH, 60 mm on both sides.

Figure 2 is an example of stress-strain data obtained by an indentation technique[25] that is ideal for small samples. The horizontal axis is the strain $\epsilon$, which is proportional to the indentation depth $\delta$ compared to the indenter's size. Here, the indenter is a flat rod with diameter $D=2$ mm. The vertical axis is the stress $\sigma(\delta)$, which is proportional to the pressure $4F/\pi D^2$ needed to force the indenter into the material with an applied load $F$. The comblike slanted lines are obtained by partial retraction and subsequently reloading of the indenter. The retraction slope reflects the material's elastic behavior. At larger strains, the material deforms plastically, as seen by the deviation from linearity in the stress-strain curve.

The proportionality factors come from theoretical considerations that have been confirmed by matching the inden-

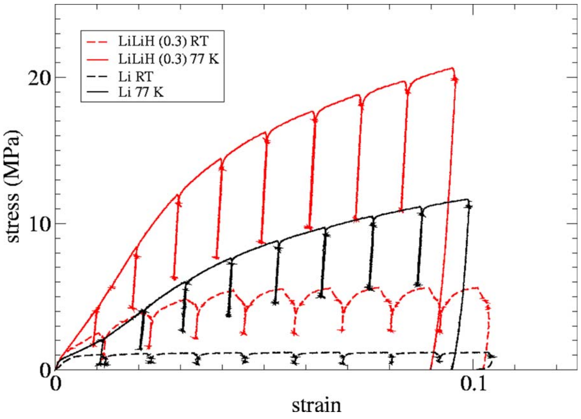

FIG. 2. (Color online) Stress-strain of pure Li and 30% LiH in Li at room temperature and at 77 K.

tation trajectory to stress-strain relationships measured by other techniques for various materials,[25] but not yet for lithium. Between materials, the proportionality factors differ at most by 25%. The relative comparison between materials in this paper is unaffected by the small uncertainty in these factors.

The black-dashed curve, for lithium at room temperature, indicates $\sigma_{\text{UTS-RT}} \simeq 1.0$ MPa for lithium's ultimate tensile stress at room temperature. The black curve, for lithium cooled to 77 K by liquid nitrogen, gives $\sigma_{\text{UTS-77}} \simeq 12$ MPa. The red-dashed curve is for Li–LiH with about 30% LiH: at room temperature, this Li–LiH composition is more than five times stronger than pure Li, with $\sigma_{\text{UTS-RT}} \simeq 6.5$ MPa. Cooling to 77 K gives $\sigma_{\text{UTS-77}} \simeq 20$ MPa, another threefold increase in strength.

With the available equipment, it was not possible to confirm the expected increase in Li's strength as function of the size of the LiH particles, e.g., as $\sigma_{\text{UTS}}(d) \simeq \sigma_0 + k/\sqrt{d}$ according to one theory.[10] Here, $\sigma_0$ is the ultimate tensile strength of the pure material, $d$ is the particle diameter, and the parameter $k$ depends on the particle's shear modulus. A systematic optimization of Li–LiH's strength as function of composition remains to be done also.

Likewise, additional measurements of the material's properties should be done to confirm the data obtained by the indentation technique. Notably, a standard pull test would also give the maximum strain $\epsilon_m$ for the various compositions of Li–LiH. A pull test on pure lithium gives $\epsilon_m \simeq 0.5$ at room temperature,[6,9] and $\epsilon_m \simeq 0.3$ at 77 K:[9] these data are used to approximate the proportionality constants that connect the load $F$ to the strength $\sigma$, and the indentation depth to the strain.

What do the material properties for Li and Li–LiH imply for soft x-ray blast windows? As discussed further below, the figures of merit appropriate for plastically deforming x-ray blast windows contain not only the ultimate tensile stress but also the maximum strain $\epsilon_m$. LiH is less ductile than pure Li, as is evident by bending a Li–LiH rod: pure Li bends easily, and the more LiH is mixed into the Li the less a Li–LiH rod bends. Unfortunately, the $\epsilon_m$ of Li–LiH samples could not be measured properly. Li–LiH's performance in soft x-ray blast windows inferred from the figures of merit that contain $\epsilon_m$, should therefore be considered tentative until further work can be done.

## IV. LI–LIH'S X-RAY TRANSMISSION

Pure lithium and pure LiH transmit soft x-rays so well that minor amounts of impurities reduce the x-ray transmission substantially. Li's mass attenuation coefficient $\mu/\rho$ is about 20 times lower than oxygen, the most likely impurity that may be introduced into Li–LiH through hygroscopic LiH powder.[13] Another worrisome impurity is sodium, whose mass attenuation coefficient is 500 times larger than lithium's. The 0.05% sodium impurity that is the maximum claimed for as-received LiH could lower LiH's x-ray transmission by 25%. Chemetall–Foote's battery-quality lithium metal is excellent for use with x-rays, with impurity levels so low that the x-ray transmission is almost ideal.

The best way to find out whether impurities affect the x-ray transmission is to measure the x-ray transmission directly. Lithium's x-ray transmission is so good that the measurement should be done with the lowest possible x-ray energy. A good choice is $h\nu \simeq 5.9$ keV, from radioactive $^{55}$Fe. For best results, the sample should both transmit and absorb an appreciable fraction of the x-rays, hence, the sample should be about an attenuation length $\ell$ thick. For pure Li the theoretical[26] attenuation length is $\ell \simeq 23.3$ mm. For pure LiH $\ell \simeq 17.1$ mm, smaller than Li's because of LiH's higher density $\rho \simeq 0.783$ g/cm$^3$ (compare $\rho \simeq 0.534$ g/cm$^3$ for Li), even though half the atoms in LiH are hydrogen that absorb x-rays even less than lithium. An artificial substance with LiH's composition and Li's density would have an attenuation length $\ell \simeq 25.1$ mm, marginally longer than $\ell$ for Li itself.

The x-ray attenuation length of as-received Li is $\ell \simeq 20.1$ mm, 7% lower than the literature value for pure Li and consistent with the material's impurities as given by the manufacturer. However, the attenuation length of the Li–LiH sample comes out as $\ell \simeq 9.9$ mm, about half of what can be expected for a mixture of Li and LiH without any impurities at the sample's intermediate density ($\simeq 0.65$ g/cm$^3$). Unfortunately, it remains unclear whether the additional x-ray absorption is caused by impurities that came with the LiH powder from the manufacturer, got into the LiH during storage outside the glovebox despite a nominally hermetic bottle, or were introduced by the manufacturing process. Here, the two principal suspects are contamination of the glovebox gas, and a reaction of liquid lithium with the stainless steel containers and/or tools.

Excessive x-ray attenuation due to impurities is of course solvable, but probably not easily. It would be most convenient if the contaminants came with the LiH powder, and if cleaner LiH powder could be purchased for a reasonable price. The worst would be if sufficiently pure LiH were not to be available, and if the necessary LiH would have to be made locally, by burning pure Li in hydrogen and subsequently, reducing the size of the resulting chunks to the desired powder.

Contamination during fabrication is not easy to avoid either. When lithium is hot enough, the liquid starts to wet the container. This suggests that the chromium oxide layer that keeps stainless steel from oxidizing further dissolves in or reacts with the liquid lithium. The result is extra oxygen in the Li–LiH mixture. Liquid lithium could also dissolve some of the carbon and nickel that are components of the container's stainless steel. Avoiding this contamination demands cups from pure iron, or from a specialty alloy that has been optimized for use with lithium: neither of these was available. Another way to minimize such contamination is to clean the cup's inside before use, by washing it with liquid lithium. The dirty lithium is discarded (or used to remove nitrogen from the glovebox), and fresh lithium can be melted in the cleaned-up cup. Whether this is effective was not tried, because with a layer of lithium adhering to the cup's walls the amount of lithium to be mixed with the LiH powder is unknown.

When the glovebox gas is clean enough, sheets of Li–

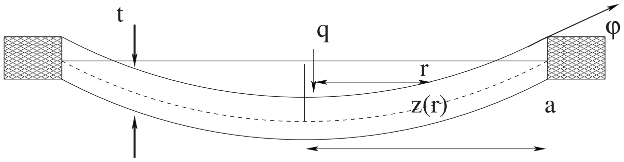

FIG. 3. Geometry for an x-ray blast shield.

LiH like the one in Fig. 1 show little sign of deterioration during storage. Absent a standard nitrogen purifier, the glovebox' nitrogen is captured sufficiently well by keeping liquid lithium at ≃225 °C in an open pan of 200 $\times 300$ mm$^2$. The pan's edge slowly develops a black crust that is removed every week or so, as needed. Sprinkling sacrificial LiH in the glovebox might remove other contaminants. Without such measures, Li–LiH corrodes noticeably faster (as seen by a color change) than lithium metal, perhaps because lithium's protective oxide layer forms water by reacting with LiH's hydrogen.[13]

## V. COMPARING MATERIALS FOR X-RAY BLAST SHIELDS

Strong plastics such as Kapton, Mylar, or Spectra are ideal materials for x-ray blast windows when the x-rays are slightly harder, with photon energy $h\nu$ closer to 10 keV or so, but the x-ray transparency of plastics is too low for the softer x-rays, say below a few keV. As already mentioned, for such soft x-rays, the best elements to be used with blast shields are beryllium, lithium, and hydrogen. Still, the various plastics can be useful to deal with practical problems. One example is lithium's oxidation in humid air. Carbon-based parylene-*N*, or perhaps other low atomic number materials, can be thin enough to transmit most of the soft x-rays, and still thick enough to be an effective humidity barrier that delays Li's corrosion. Barrier layers are ignored in the strength estimates that follow.

As already mentioned, the comparison between Li–LiH and other soft x-ray window materials is tentative: for a definite assessment, more work is certainly needed, to optimize the composition of Li–LiH, to measure all its relevant mechanical properties, and to suppress the impurities that cause excessive x-ray absorption. However, for designing actual x-ray windows, there issues are less important than the many shortcuts taken in the window's mathematical model: an actual soft x-ray window is a two-dimensional structure differentially heated and impacted by a dynamic pressure, while the analysis assumes a long, one-dimensional foil under static pressure. The simplification to one dimension is not particularly serious because it affects only some proportionality constants. However, the window's mass per unit area could be important if it responds dynamically, the material strength should include strain rate effect, and also the pulse shape and the attachment geometry can become relevant. The simplified analysis should be sufficient for the purpose here, to highlight nonstandard choices for x-ray window materials such as lithium and its strengthened variants by comparing their figures of merit to those of the standard, beryllium.

Figure 3 is the simplified x-ray window geometry. A one-dimensional membrane is held at its edge by a fixed support at $r=a$. Its deflection is described by the deflection $z(\xi)$ normalized to the half width $a$ as function of the normalized distance $\xi=r/a$. At the edge, where $\xi=1$, the deflection $az(1)=0$: in the center where $\xi=0$, the deflection $az(\xi)$ is largest. The figure suggests a typical value for the normalized deflection, $z(0)\simeq 0.2$. The sag in the center implies that the window material lengthens, from $a$ to $a(1+\epsilon)$. For the relatively small deflection of a one-dimensional window as in Fig. 3, the strain is approximately $\epsilon \simeq \sqrt{1+z^2(0)} \simeq 1 + z^2(0)/2 = 0.02$. For cylindrical, rectangular, or square windows, the strain is on the same order as in one dimension (and larger for the square than for the circle). A similar factor that accounts for shrinking of the window thickness described by Poisson's ratio is likewise ignored.

For a proper comparison, all the x-ray windows must have the same x-ray transmission $T$ irrespective of the material. The transmission of a usable soft x-ray window must of course be excellent, perhaps up to $T \simeq 0.9$, so that an actual window is probably much thinner than shown in Fig. 3. In such membranes the force is along the material, in the one-dimensional approximation in the direction $\partial z/\partial\xi$: bending forces and the complications associated with thick materials are therefore ignored.

Different materials have the same x-ray transmission $T$ when their thickness $d$ is the same in units of attenuation length $\ell$: $T=\exp(-d/\ell)$. In what follows, the window thickness is chosen to be one attenuation length, $\ell_5$, at a particular photon energy, $h\nu=5$ keV. This choice gives convenient numerical values for the various quantities, and it is close to the energy (5.9 keV) with which the attenuation length is measured on the 11.3 mm thick samples.

A vertical sheet of material that hangs down under its own weight supports a maximum force per unit length $\gamma_0 = \ell\sigma_{\mathrm{UTS}}$, so that $\gamma_0$ is a good figure of merit for the material in such a sheet. It is relevant for x-ray window materials when the geometry remains the same, as it does when the strain is small compared to unity. For convenience, the subscript on the ultimate tensile strength, $\sigma_{\mathrm{UTS}}$, is dropped from now on.

In contrast, when the material is very ductile and the maximum strain $\epsilon_m$ is relatively large, the window's shape can change appreciably, enough to modify the pressure it can withstand. Hence, the two other figures of merit to be derived below contain the material's $\epsilon_m$.

A flat membrane supports a lower pressure than a membrane that is preformed as part of a sphere. The basic $\gamma_0$ also applies to such a preformed structure. This is easiest to see for a two-dimensional hemisphere (which is not a good shape for an x-ray window). A hemisphere with radius $a$ under a pressure $q$ exerts a force $F=q\pi a^2$ over its area $\pi a^2$. This force is taken up by the hemisphere's circumference, with length $L=2\pi a$. Per unit length the force is then $f = F/L = qa/2$. The same situation in one dimension is a long cylinder held on two rails parallel to the cylinder's axis a distance $2a$ apart, as in Fig. 3. Omitting end effects, a pressure $q$ exerts a force $F=2a\Delta Lq$ on the cylinder for a length $\Delta L$ along the cylinder, and the force per unit length $f=2aq$. A material that can support a maximum force per unit length

TABLE I. Some approximate material properties and the resulting figures of merit for x-ray window materials. $\gamma_0$ is for a straight sheet, $\gamma_e=\gamma_0\sqrt{\sigma/E}$ for the standard membrane, and $\gamma_p=\gamma_0\sqrt{\epsilon_m}$ for a membrane with large deformation.

| Material | $\ell_5$ (mm) | $E$ (GPa) | $\sigma$ (MPa) | $\epsilon_m$ | $\gamma_0$ (kN/m) | $\gamma_e=\gamma_0\sqrt{\sigma/E}$ (kN/m) | $\gamma_p=\gamma_0\sqrt{\epsilon_m}$ (kN/m) |
|---|---|---|---|---|---|---|---|
| Be (RT) | 1.27 | 300 | 258 | 0.008 | 328 | 9.6 | 29 |
| Li (RT) | 14.3 | 11.4 | 1.0 | 0.5 | 14 | 0.13 | 10 |
| Li (77 K) | 14.3 | 11.4 | 12.0 | 0.3 | 172 | 5.6 | 94 |
| Li–LiH (RT) | 10.8 | 11.4 | 6.5 | 0.2 | 70 | 1.7 | 30 |
| Li–LiH (77 K) | 10.8 | 11.4 | 20.0 | 0.1 | 216 | 9.0 | 70 |
| Spectra | 0.51 | 95.0 | 2000 | 0.03 | 1020 | 148 | 177 |

$\gamma_0$ then withstands a maximum pressure $q_m=2\gamma_0/a$ if it is a preformed as a hemisphere, but preformed as a cylinder it withstands only $q_m=\gamma_0/2a$. The dimensionality of the situation comes in as a simple factor, 2 for the two-dimensional hemisphere and $1/2$ for the one-dimensional cylinder, but such a factor does not affect the comparison between materials in the same geometry.

X-ray windows are never hemispheres or half cylinders, but they could be hemispherical sectors that attach to their support under a fixed angle $\theta$ with the support's plane. A full hemisphere has $\theta=\pi/2$, and $\sin\theta=1$, but for a good x-ray window, the hemisphere should be shallow, with $\theta=(\partial z/\partial\xi)\ll 1$. The force per unit length perpendicular to the support remains the same, $f=qa/2$, but the force along the membrane increases by the factor $1/\sin\theta$. The maximum pressure supported by a shallow hemispherical membrane is correspondingly smaller, $q_m=\gamma_0\sin\theta/2a$.

A completely flat membrane without tension does not support any pressure. Instead, the smallest pressure bows the membrane out until it reaches an angle $\theta$ with $\sin\theta=2qa/\gamma_0$, or until it bursts from too much strain. The simple figure of merit $\gamma_0$ can therefore apply to more or less realistic geometries, when the window is a preformed hemispherical shell whose angle at the support $\theta=(\partial z/\partial\xi)$ is a constant. This implies that the strain be small enough to keep the geometry essentially unchanged, despite the pressure. It should be no surprise that the dimension of $\gamma_0=\ell\sigma$ is the same as surface tension: in fact, surface tension was originally analyzed as a thin membrane.

Table I gives some numbers for beryllium, lithium, and a typical composition of Li–LiH, at room temperature and at 77 K. For Li–LiH, the table gives the theoretical value[26] for the attenuation length of LiH, although this is almost twice as large as the measured value for the material produced to date: suppression of LiH's contamination should give close to the theoretical x-ray attenuation, as is, indeed, the case for pure lithium metal by itself. Likewise, the mechanical data for Be and Li are from the literature, while those for those for Li–LiH are the provisional data inferred from the impression tests.

Values for the basic, small-strain figure of merit $\gamma_0$ are given in the table's fifth column. Beryllium's $\gamma_0$ is the largest, but not by much: it is only about 50% larger than for uncontaminated Li–LiH at 77 K: cryogenically cooled lithium metal by itself is about half as good as beryllium. Even at room temperature, uncontaminated Li–LiH would still be reasonably strong, with $\gamma_0\simeq 0.2$ of beryllium's $\gamma_0$. Room temperature lithium is, of course, mechanically weak, as seen in its low $\gamma_0$.

Table I also gives two other figures of merit. One, $\gamma_e$, applies to the conventional situation of an initially flat but elastic membrane on a rigid support. Various standard compilations[27] give basically the same expression for the maximum pressure, $q_{\max}\propto C\ell\times\sigma^{3/2}/\sqrt{E}$. Here, $C$ is a constant that depends on Poisson's ratio and $E$ is Young's modulus. Besides the membrane approximation, the derivation assumes that the normalized deflection $z(0)$ is small compared to unity, and that the material remains elastic, i.e., the maximum strain $\epsilon_m=E/\sigma$. In terms of $\gamma_0$, the maximum pressure is $q_{\max}\propto C\gamma_0\sqrt{\sigma/E}$, so that the appropriate figure of merit for a rigidly supported, flat membrane within the linear elastic regime is $\gamma_e=\gamma_0\sqrt{\sigma/E}$.

The extra dimensionless quantity $\sqrt{\sigma/E}$ in $\gamma_e$ comes from the angle $\theta$ that the membrane develops with respect to its initially flat position. As already mentioned, in a one-dimensional geometry, the strain is connected to the normalized deflection by $\epsilon\simeq z^2(0)/2$: the same quadratic expression applies for a circular membrane except for the factor that multiplies $z^2(0)$ (here, $1/2$). A membrane under pressure bows out with an angle $\theta$ that is proportional to $z(0)$, and therefore, proportional to $\sqrt{\epsilon}$. In essence, the factor $\sqrt{\sigma/E}$ is the inverse of $\theta$.

The values for $\gamma_e$ in Table I are about equal for beryllium and for uncontaminated Li–LiH cooled to 77 K, while cryogenically cooled lithium gives about half this value. Cryogenically cooled Li–LiH would then be equivalent to beryllium if the contamination problem were resolved.

A third figure of merit is $\gamma_p=\gamma_0\sqrt{\epsilon_m}$. This is the same formula for a material that remains elastic, $\gamma_e$, but valid for a very plastic material with a very small elastic regime. The relevant example here is lithium. Stretching a plastic material is often described by a nonlinear relation between stress and strain, $\sigma(\epsilon)$, with an elastic region wherein $\sigma(\Delta\epsilon)\simeq(\partial\sigma/\partial\epsilon)\Delta\epsilon$ over a small region of strain close to zero, $\Delta\epsilon\ll 1$. Failure occurs at some maximum strain $\epsilon_m$, which can be much larger than $\Delta\epsilon$ and not necessarily small compared to unity. The ultimate tensile stress is then $\sigma_{\mathrm{UTS}}=\sigma(\epsilon_m)$. A plastic material can have its $\sigma_{\mathrm{UTS}}/\epsilon_m$ much smaller than the corresponding value in the elastic regime, Young's modulus $E=(\partial\sigma/\partial\epsilon)$ at zero strain. The extra factor $\sqrt{\epsilon_m}$ in $\gamma_p$ is again from the angle $\theta$, this time, estimated for maximum plastic strain.

In Table I, the maximum strains quoted for Be and Li are from the literature, and the maximum strain for Li–LiH is taken to be half that of Li: a proper measurement remains to be done.

Judging from $\gamma_p$ for plastic deformation, beryllium seems not as good in x-ray windows as lithium at 77 K might be. The reason is lithium's large increase in strength on cooling, by an order of magnitude, while the maximum strain decreases only by a factor of 2. The estimate for $\epsilon_m$ suggested in the table yield values for $\gamma_p$ that exceed beryllium's $\gamma_p$, but note that $\gamma_p$ for Li–LiH is provisional: its maximum strain is estimated, not yet measured.

Table I also gives data for one particularly promising plastic, a linearly stretched polyethylene known under the trade name Spectra. An x-ray window made from Spectra would exceed all the low atomic number elements, in all three figures of merit. Unfortunately, Spectra cannot be directly compared to the other materials, for two reasons. Spectra absorbs x-rays more readily than the other materials, so that x-rays could easily heat Spectra so much that it loses strength: Spectra remains strong up to 70 °C only. In addition, Spectra does not come as a foil with the same strength in all directions, but only as a unidirectional fiber. To use Spectra as an x-ray window, it must be woven into cloth and the remaining holes sealed with one of the other materials. For this reason, Spectra may well be an ideal material for a support grid that makes an x-ray window from lithium or Li–LiH stronger than it would otherwise be. Such a support grid would require good enough heat contact between Spectra's fibers and the cool lithium to keep Spectra's temperature below 70 °C.

In practice, the material used in an actual soft x-ray blast window may be selected not only on the basis of these various figures of merit only but also on factors such as availability and price. For example, it may be too expensive to have a foil made from beryllium that is large enough for the desired experiment and still thin enough to get the desired x-ray transmission. Lithium comes in wide (120 mm), thin (0.1 mm) ribbons, which can be stitched together to form arbitrarily large areas (simply by pressing the ribbons together after cleaning: lithium is not only ductile but also sticky). To be practical, such a large lithium blast window may have to be strengthened with a support grid, e.g., from Spectra.

## VI. CONCLUSION

The data in Table I suggest that designers of survivable x-ray windows might profitably consider other materials than only beryllium: the various figures of merit, which should be considered provisional until more work can be done, are close enough to each other that no single material jumps out (except for Spectra). The utility of Li–LiH is bound to improve with further development, through optimized composition, more uniform and smaller particles of LiH, and, of course, the necessary suppression or avoidance of contaminants.

Lithium by itself already does well as a survivable but nonreusable, plastically deforming x-ray window in a vacuum, especially when cooled to 77 K. This relatively minor amount of cooling is easy to accomplish with a minimum of cryogenic engineering. Therefore, lithium or Li–LiH may well be the preferred material for disposable soft x-ray windows, especially where beryllium is prohibited for health reasons, or when complying with the regulations that govern beryllium's use is too cumbersome. Lithium and Li–LiH have their problems, but for these problems the solutions are technical and more pleasant to deal with than addressing beryllium's safety-related issues.

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