Pressure present during metallization of xenon

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Enormous pressure intensification occurs due to plastic deformation of thin films between anvils. In the present paper, simple plasticity theory is used to illustrate this; it leads to excellent agreement with experiments. The results of this analysis are then used to show that the pressure present in solid xenon when it exhibited electrical conductivity was much greater than given by Nelson and Ruoff [Phys. Rev. Lett. 42, 383 (1979)]. This pressure was, so far as the evidence of the present analysis shows, above 1 Mbar.

Nelson and Ruoff[1] squeezed solid xenon at 30 K to high pressures and observed that the xenon changed from an electrical insulator to a conductor. In their procedure, interdigitated electrodes were produced on the flat diamond anvil using lithographic methods. This anvil was placed in a vacuum chamber and, after evacuation, was cooled to about 30 K. A thin film of xenon was next depostied on this anvil; the film thickness was measured using a quartz-crystal thickness monitor. Next, a diamond with a spherical tip was pressed against the xenon film. Using a tip with a 50-μm radius, they found that a rapid drop in the measured resistance began at a force (on the average) of 144 g. Because of the nonshorting configuration of the interdigitated electrodes, this resistance drop is interpreted as evidence for the transition of xenon from an insulator to a conductor.[1] They than made the *assumption* that the pressure generated in the thin sample was the same as when the spherically shaped diamond tip was pressed with the same force directly onto the flat diamond (with no electrodes or sample present). This led to the conclusion that xenon was a conductor at a pressure of only 330 kbar. We note in the present paper that a large concentration of pressure occurs in the sample as a result of plastic deformation and that the pressure in the xenon sample is, in fact, much higher than Nelson and Ruoff stated. Thus their results are not inconsistent with the prediction of Ross and McMahan[2] that the band gap of xenon would go to zero at a pressure of at least 1.3 Mbar.

The intensification which occurs due to plastic flow in a slightly different geometry has been studied in detail both experimentally and theoretically. Experiments have been carried out by Hoeckstra *et al.*[3] using the ruby method[4] to measure the mean normal stress as a function of radius for various reductions in thickness of a circular disc of aluminum squeezed between two large blocks of transparent sapphire with parallel faces (the faces of the blocks are much larger than the area of the circular disc). The stresses present in the aluminum disc have also been computed by Hoeckstra *et al.*[3] using the MARC general purpose finite element computer program.[5] This allowed treatment of fairly large plastic strains, elastic strains, and strain hardening. They also obtained the true tensile stress-strain curve for the aluminum they used. Recently, Chan *et al.*[6] have used a simpler model of plasticity to compute the stress distribution when plastic flow occurs.

In Table I, we compare the maximum mean normal stress (at $r=0$) for various reductions in thickness found by experiment,[3] by sophisticated plasticity theory,[3] and by simple theory.[6] Note the enormous pressures predicted for very large reductions in thickness, i.e., a pressure of over 300 kbar for a reduction of 95% for a disc (of dimensions $r_0 = 4$ mm, $h_0 = 2$ mm) made of material whose initial yield stress was about 0.25 kbar!

When such high pressures are obtained (at very large a/h), it is necessary to consider the effect of the pressure (the mean normal stress) on the flow stress itself. This effect becomes very important when the pressure reaches a significant fraction of the bulk modulus at zero pressure, B_0. There are theoretical reasons why the flow stress should scale with pressure in the same way as some effective elastic constant does.[7]

Using the same simple plasticity theory, Chan *et al.*[6] obtain

$$\sigma_m(r) = \frac{C_0}{C_0'}\left[\left(1+\sigma_m(a)\frac{C_0'}{C_0}\right)\exp A\left(1-\frac{r}{a}\right)-1\right] , \tag{1}$$

where

$$A = \frac{\sigma_{00} a C_0'}{h[1-\frac{1}{3}\sigma_{00}(C_0'/C_0)]C_0} . \tag{2}$$

Here, σ_m is the mean normal stress, a is the radius of contact, r is the radius, C_0 is the appropriate elastic constant at zero pressure, C_0' is the pressure derivative of this elastic constant at zero pressure,

TABLE I. Maximum values of mean normal stress in kbars.

% reduction in thickness	von Mises flow stress[a]	Present simple theory	Experiment[b]	Sophisticated theory[b]
10	0.83	2.2	1.8	1.9
25	1.09	3.7	3.4	3.5
40	1.27	5.9	5.4	6.0
55	1.44	10.0	9.8	c
65	1.55	15.5	14.8	c
90	1.91	122	. . .	. . .
95	2.05	368	. . .	. . .

[a]Computed as discussed in Ref. 6. The initial flow stress of the aluminum was about 0.25 kbar.
[b]Reference 3.
[c]Strains were too large to handle; mesh became too distorted.

σ_{00} is the compressive yield stress at zero pressure, and h is the film thickness under load.

Although Nelson and Ruoff squeezed xenon between a diamond with a spherical tip and flat diamond, we shall assume that h does not vary with r in their experiment (in which case the above equations apply); thus the results are only approximations.

For xenon, we use the available bulk modulus value for C_0 and C_0' of Syassen and Holzapfel.[8] We use, for the condition of Nelson and Ruoff, $B_0 = 33.0$ kbar, and for C_0' we use $B_\infty' = 4.80$. The use of B_∞' assures that the scaling factor is a lower bound based on the bulk modulus. For the value of a, we use the contact radius which would have existed for diamond against diamond for a tip radius $R = 50$ μm,[1] so $a = 4.5$ μm. We use $h = 0.072$ μm, which is a 60% reduction in thickness from the initial film thickness. Towle gives $\sigma_{00} = 0.25$ kbar without strain hardening.[9] We use $\sigma_{00} = 0.55$ kbar to partially account for strain hardening. (Note that σ_{00} for the aluminum discussed earlier increased from about 0.25 to 0.83 kbar as a result of a reduction in thickness of 10%.) Finally, we obtain $\sigma_m(a)$ by setting $\sigma_r(a) = 2\sigma_{00}$, which is discussed elsewhere.[6] We then have

$$\sigma_m(0) = 8.16 \exp 5.14 = 1390 \text{ kbar} \quad . \tag{3}$$

We believe that the value of a and σ_{00} may be larger than those used so the exponent may be even larger. We do not intend this as a quantitative result. Obtaining a quantitative result would require the use of sophisticated plasticity theory, including the use of the exact shape of the tips, elastic deformation of the tip and anvil, etc. It would be a very different problem, indeed. The important point we wish to make is that the stress distribution given by Eq. (1) is drastically different from that of the Hertz situation for diamond against diamond where the distribution is hemisperhical, i.e.,

$$P(r) = P_0(1 - r^2/a^2)^{1/2} \quad , \tag{4}$$

where $P(r)$ is the pressure at radius r, P_0 the pressure at the center, and a the radius of the contact region. The actual distribution of stresses with a soft sample present is much steeper than this. [However, we wish to point out that the pressure distribution of Eq. (1) exhibits a cusp at $r = 0$; we believe that no cusp exists and that the slope goes to zero at $r = 0$.] We have to conclude that the maximum pressure exerted in xenon in the experiments of Nelson and Ruoff is considerably higher than the 330 kbar given by them based on the Hertz relation for P_0 and the assumption that the pressure distribution is the same as for diamond against diamond.

Thus the Nelson and Ruoff[1] results are not inconsistent with the theoretical results of Ross and McMahan[2] who predict band-gap closure at a pressure of at least 1.3 Mbar, or the experiments of Schiferl[10] who noted no color change in xenon at 440 kbar, and of Syassen[11] who noted that the band gap of xenon was 3.9 eV at 440 kbar. Both of the latter pressures are based on the ruby scale.[4]

Note added in proof. Since this paper was written, two other relevant studies on xenon by Asaumi, Mori, and Kondo[12] and Makarenko *et al.*[13] have come to our attention. In both cases the band gap is similar to that found by Syassen,[11] so that band-gap closure is expected above 1 Mbar, consistent with the present conclusion.

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