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The inversion of relative shear rigidity in different material classes at megabar pressures

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Abstract

The behaviour of elastic moduli of substances is analysed in the megabar pressure range. A new effect—inversion of the shear moduli and mechanical properties upon compression—is predicted for various classes of substances. The melting-curve data for different materials confirm the predicted phenomenon. The materials traditionally considered the softest, such as rare-gas solids and molecular substances, may become the hardest in the megabar range. This should be taken into account in developing experimental high-pressure techniques.

1. Introduction

Studies of the behaviour of elastic properties and mechanical characteristics of strongly compressed materials are of crucial importance both to fundamental physics and geology and as regards high-pressure techniques. In the quantum pressure range $P > Z^{10/3} m^4 e^{10} / \hbar^8 \sim 10^2\text{--}10^5$ Mbar corresponding to a compression ratio that is a (small) multiple of ten, all properties of a substance, including its elastic moduli, can be thought of as being monotonic and almost linear functions of the atomic number [1]. It is known that in the experimentally attainable megabar pressure range corresponding to a compression ratio that is a small number, the properties of substances are, generally, nonmonotonic functions of the atomic number [1, 2]. At the same time, it is *a priori* unclear whether the materials will still be divided into hard and soft in the megabar range, and which classes of substances will have the highest elastic moduli, hardness, strength, etc, at such pressures.

It should be emphasized that the determination, by both experiment and computer simulation, of the mechanical properties such as hardness and strength for substances under pressure is a highly challenging task. It is known, however, that these properties are closely related to the shear rigidity of the materials and, correspondingly, to their elastic moduli [3], which, in turn, are uniquely defined physical characteristics of substances. Therefore, the purpose of this work was to analyse the elastic behaviour—primarily the shear moduli—of

substances in the megabar pressure range on the basis of available experimental data and model empirical approaches. We will restrict our consideration mainly to rare-gas solids and metals, because these classes are precisely the ones for which the predicted effect is expected to be most pronounced.

At normal pressure, the bulk and shear moduli of various substances lie in the range from kilobars to megabars [4, 5]. On compression, the elastic moduli increase (except for the possible anomalous behaviour near phase transitions). For most substances, the experimentally measured pressure derivatives of the bulk and shear moduli range from 1 to 8 [4, 5]. Consequently, the elastic moduli at megabar pressures are more likely to be determined by the corresponding pressure derivatives rather than by the initial values of the moduli. At pressures of 3 Mbar and higher, the elastic modulus, for every substance, is higher than that of diamond at normal pressure, the ‘record holder’ among all materials. As a result, there are no soft (in the ordinary sense) substances in the megabar range.

2. Method

The behaviours of the bulk moduli of the majority of substances have been much studied up to megabar pressures [1, 2]. By contrast, the shear moduli of the majority of substances have been measured only up to pressures of several tens of kilobars [4, 5]. As regards the megabar range, only indirect approximations are known for the behaviours of the elastic shear constants of some substances, including Ar and several metals (Fe, Au, and Mo) [6–8]. At the same time, the behaviours of elastic constants of various classes of substances at high pressures can be analysed by using a simple model of a system of particles interacting via the power- n –power- m potential $U = A/r^n - B/r^m$. With increase in pressure, the effective repulsion exponent n , lying in the interval from 6 to 12 for the majority of substances, becomes dominant. This is so because the relative contribution to the elastic moduli and pressure from the noncentral forces, energy of valence electrons, and interior Coulomb forces, as well as from the attractive forces (the $-B/r^m$ term in the power- n –power- m potential) rapidly drops upon compression, as compared to the contribution from the central repulsive forces between nearest neighbours [9].

In this paper, we restrict consideration, for brevity, to the analysis of an FCC lattice that corresponds to one of the close-packed atomic arrangements. For the elementary cubic (simple cubic, BCC, and FCC) lattices with central interactions between atoms, one can readily obtain general expressions for the pressure and elastic constants [9, 10]:

$$P = \frac{1}{v} \sum_{R_i} [U'_{r^2} r_x^2]_{R_i}, \quad (1)$$

$$c_{11} = \frac{2}{v} \sum_{R_i} [U''_{r^2} r_x^4]_{R_i} - P, \quad (2)$$

$$c_{12} - P = c_{44} + P = \frac{2}{v} \sum_{R_i} [U''_{r^2} r_x^2 r_y^2]_{R_i} \quad (3)$$

where v is the unit-cell volume, the sums are over the lattice vectors R_i , and the derivatives of the interaction potential are taken with respect to the r^2 -variable: $U'_{r^2} = dU(r^2)/d(r^2)$, etc.

3. Results and discussion

The expressions obtained in this work for the derivatives of the bulk and shear moduli of a lattice with a purely repulsive potential $U = A/r^n$ in the short-range (soft-sphere)

Table 1. The pressure derivatives of the elastic constants for the FCC lattice with the repulsive power-law potential $U = A/r^n$ (the relations $B' = B/P$ and so on are valid in this case). The shear moduli were calculated in the approximations of Voigt, $G_V = [9c_{44} + 3(c_{11} - c_{12})]/15$, and Voigt, Reuss, and Hill, $G_H = (G_V + G_R)/2$, where $15/G_R = 12/(c_{11} - c_{12}) + 9/c_{44}$. For each variable, the first row in the table corresponds to the nearest-neighbour interaction, whereas the second row gives the interpolation ($5 \leq n \leq 15$) to the ordinary case of long-range interactions. The expressions for B' and G'_V are the same in both cases. The pressure is normalized by a factor U_a/d^3 , where d is the nearest-neighbour distance and $U_a = A/d^n$ is the nearest-neighbour interaction energy.

Pd^3/U_a	$2n\sqrt{2}$ $\approx 13.18 + 0.762n + 0.0822n^2$
B/P	$(1/3)n + 1$
$\frac{1}{2}(c_{11} - c_{12})/P$	$(1/8)n - 3/4$ $\approx -0.23 + 0.056n + 0.0024n^2$
c_{44}/P	$(1/4)n - 1/2$ $\approx -0.85 + 0.296n - 0.0016n^2$
G_V/P	$-3/5 + (1/5)n$
G_H/P	$(53/280)n - 669/980 - 120/(343n - 1274)$ $\approx -0.53 + 1.061n + 0.0011n^2$

and long-range interaction models are given in table 1. Note that the bulk modulus of a lattice with central interaction is related to Voigt's shear modulus by the exact expression that follows from the Cauchy relation including pressure [11]: $c_{12} = c_{44} + 2P$. Indeed, $G_f = (9c_{44} + 3(c_{11} - c_{12}))/15 = ((c_{11} + 2c_{12}) - 6P)/5 = (3/5)B - (6/5)P$. The derivatives with respect to pressure are also obtained from these expressions:

$$G'_f = (3/5)B' - 6/5. \quad (4)$$

It is significant that the derivatives of the elastic moduli and the relative shear elasticity of a lattice, $G/B \approx G'/B'$, both increase with n at ultrahigh pressures. The same trends hold in the general case of the power- n -power- m potential (figure 1). With rise in pressure, the derivatives of the elastic moduli of a lattice with a power- n -power- m potential tend to their soft-sphere ($U = A/r^n$) values (figure 2). For compressions $V/V_0 \sim 0.5$ (which correspond to real substances under pressures from tens of kilobars to a megabar [1]), they differ from the limiting values at $V/V_0 \rightarrow 0$ by no more than 5–20%. That is, in the high-pressure limit ($P \rightarrow \infty$), one has $G'_f(\infty)/B'(\infty) = (3/5)(n-3)/(n+3)$. At the same time, it follows from equation (4) that, in a lattice with central forces (or, approximately, in any lattice at ultrahigh pressure), $\Delta(G'_f)/\Delta(B') = 3/5$ for any change in pressure. It then follows that the ratio $(\Delta(G'_f)/\Delta(B'))/(G'_f(\infty)/B'(\infty)) = (n+3)/(n-3)$ always exceeds unity and decreases with increasing n . Therefore, with rise in pressure, the relative change in the derivative of the shear modulus is always larger than that in the derivative of the bulk modulus, the effect becoming more pronounced with decrease in the exponent n of the repulsive potential. Poisson's ratio in the high-pressure limit is equal to $\sigma = (n+7)/(4n+8)$.

One can draw the following important conclusion from the above analysis. If the elastic moduli of one of (any) two substances are lower at normal conditions but its interatomic repulsive potential is more rigid (the effective exponent n is larger), then the ratios of the moduli of these substances will be inverted under pressure and the final difference between their shear moduli will always be higher than that between their bulk moduli. Evidently, the physical reason for such effects is associated with the negative contribution of pressure to the shear moduli [2, 10]—in particular, to the constants $(c_{11} - c_{12})/2$ and c_{44} for the cubic lattice (see equations (2) and (3))—and is formally clarified by equation (4).

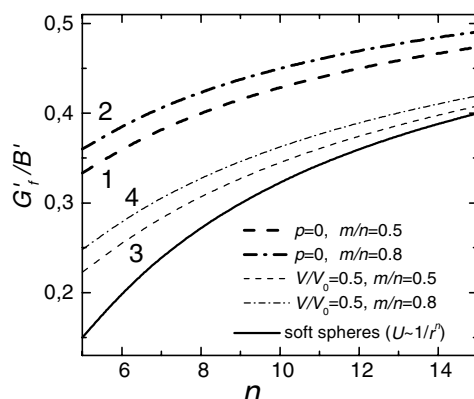


Figure 1. The G'_f/B' ratio as a function of the repulsion exponent n for the FCC lattice with a power- n -power- m potential. ((1), (2)) $P = 0$ and $m/n =$ (1) 0.5 and (2) 0.8. ((3), (4)). The pressure corresponding to $V/V_0 = 0.5$ and $m/n =$ (3) 0.5 and (4) 0.8. The data for the soft-sphere model with the $1/r^n$ potential (see table 1) correspond to the power- n -power- m potential ($m < n$) at $P \rightarrow \infty$.

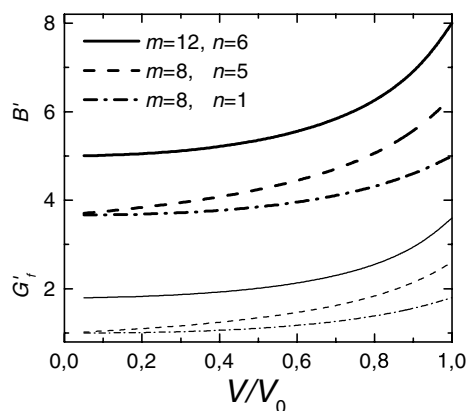


Figure 2. The pressure derivatives of the bulk modulus (thick curves) and Voigt's shear modulus (thin curves) as functions of the compression ratio for the FCC lattice with power- n -power- m potentials typical of rare gases ($n = 12$ and $m = 6$) and d metals [13].

Clearly, real substances are not described by the simple power- n -power- m potential. However, one can draw from the above analysis qualitative conclusions about the relative behaviour of elastic properties of various classes of substances under strong compression. In particular, the effective interatomic potential in metals is softer than that in rare-gas solids. The effective repulsion exponent n in metals is smaller because of the screening effect of free valence electrons. One can naturally expect the inversion of shear moduli and, correspondingly, of other mechanical characteristics of these two classes of substances, in view of the fact that rare-gas solids are exceedingly soft substances at low pressures. Note that simple estimates from equations (1)–(3) yield quite realistic values for the derivatives of elastic moduli under pressure. For instance, the B' -value of rare-gas solids ($n \approx 10$ – 12 and $m \approx 6$) should change from 7–8 to 4–5, G' from 3.2–3.6 to 1.4–1.8, and σ from 0.25 to 0.34, in good agreement with experimental data [8, 12, 13]. For transition metals, one can set $n \approx 8$ and $m \approx 3$ [14].

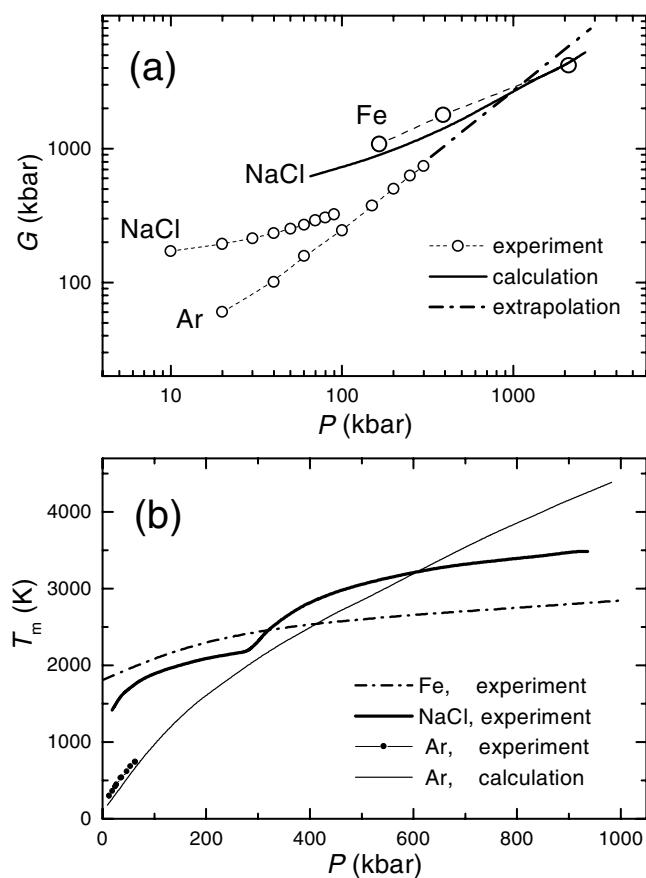


Figure 3. Pressure dependences of the (a) shear moduli and (b) melting temperatures for typical representatives of the rare-gas solids (Ar), the alkali halide compounds (NaCl), and the metals (Fe). The experimental shear moduli are taken from [6] for Fe or calculated from the experimental elastic constants for Ar [12] and NaCl [14]. The shear modulus of NaCl (with the CsCl structure) is estimated from the theoretically calculated values of $(c_{11} - c_{12})/2$ [2]. The theoretical melting curve for Ar is taken from [1], and the experimental curves are taken from [16] for Fe and NaCl (interpolations) and from [21] for Ar.

Accordingly, the B' -value should change from 5.5 to 3.7, G' from 2.2 to 1, and σ from 0.3 to 0.4, also in good agreement with experiment [4–7]. These estimates are also confirmed by other empirical calculations. The expression suggested in [5] gives $G' \sim 1.3 \pm 0.3$ for metals and $G' \sim 1.9 \pm 0.4$ for rare-gas solids at megabar pressures. Lattice calculations with a more exact interaction model give $G' \approx 2$ for rare-gas solids at $P \sim 0.5$ Mbar [2].

At a pressure of several megabars, the shear moduli of metals probably become several tens per cent smaller than in rare-gas solids (except, perhaps, He), whereas the bulk moduli of metals become either close to or 10–50% higher than the values typical for rare-gas solids. The fact that the B' - and G' -values of He, Li, LiH, and, probably, metallic hydrogen are smaller than those of the other substances of their classes is caused by the absence of inner-core electrons and by the soft repulsive potentials in these materials. At relatively low pressures, the derivatives for alkaline and some alkaline-earth metals are also small, $G' \sim 0.5$ –1 [4, 5], and, accordingly, the shear moduli are several times lower than for other substances. However,

after the electronic and phase transitions occurring in the pressure range from 50 kbar to 1 Mbar, the G' -values of these substances should become close to the values for other metals.

The currently known empirical calculations and available experimental dependences do not contradict our hypothesis of the inversion of shear moduli in substances of various classes (figure 3(a)). Moreover, some indirect facts support this suggestion. Within the framework of the Lindemann melting criterion, the pressure behaviour of the melting temperature T_m is primarily governed by the behaviour of the shear modulus, as is also confirmed by experimental data [16].

As distinct from the shear moduli, the melting temperatures have been experimentally measured or calculated *ab initio* for a series of substances of different classes up to pressures of several megabars. It turns out that the melting curves of metals in the megabar pressure range become flatter than those of nonmetals [17–19]. The melting curves of inert substances such as Ar and of alkali halide crystals such as NaCl intersect the melting curves of metals, e.g., Fe (figure 3(b)). The intersection of the melting curves is a remarkable confirmation of the hypothesis of inversion of shear moduli of the corresponding classes of substances.

The results obtained in this work may find an important practical application to high-pressure techniques in the problem of choosing between various substances as pressure-transmitting media. At room temperature and pressures higher than 120 kbar, all substances are solids. In particular, helium crystallizes and alcohol mixtures undergo the glass transition. Nevertheless, the experimentalists working in the megabar pressure range traditionally use solidified organic liquids or rare-gas solids as working media at high pressures. In doing so, they unjustifiably extend the conclusion of the softness of these substances to the megabar pressure range. As was pointed out above, no soft substances occur in the megabar range: the shear moduli of all materials are equal to several megabars and, accordingly, their flow stresses $\sigma_y \sim (0.05\text{--}0.1)G$ (see [20] and references cited therein) are equal to hundreds of kilobars. The ratio between the characteristics of different substances is an important parameter.

It follows from the predicted inversion of elastic moduli that, starting at certain pressures, the shear rigidities (hardness, strength, etc) of rare-gas solids (except perhaps He) should be higher than the same characteristics for metals and alkali halide crystals (figure 3). Also, the σ_y/G ratio for metals should be lower because of their high plasticity. Indeed, it is known from experimental studies that Ar becomes stiffer than iron and steel at pressures above 1.5 Mbar [21], and Xe becomes stiffer than CsCl at pressures of hundreds of kilobars [22]. Solidified organic carbon-containing liquids polymerize at 50–400 kbar to form diamond-like sp^3 bonds. This should lead to a rapid increase in the shear moduli and hardness up to levels close to those for diamond. As a result, starting at several hundreds of kilobars, it makes no sense to use organic liquids as the quasi-hydrostatic medium, because they are stiffer at these pressures than practically all materials under investigation. Thus, the materials that are stiff at normal pressure (metals and ionic insulators) are preferable for use as soft quasi-hydrostatic media in the megabar pressure range. Transparent materials such as alkali halide crystals, and hydrogen-containing compounds such as H₂O ice and NH₃ (ammonia), are suitable for use in optical studies. Note that, although experimental data on the shear modulus of H₂O ice at $P > 100$ kbar are lacking, the melting-curve data for H₂O [23] allow one to assume that ice, along with LiH, becomes one of the softest materials (probably softer than helium) at $P \sim 2\text{--}3$ Mbar. Indeed, the ionic crystals KBr and NaCl have found use in recent years as pressure-transmitting media in megabar experiments. In many cases, it is reasonable to use the appropriate metals, including In, Pb, Sn, Na, Be, Bi, Ga, etc (Li is unsuitable because of its active diffusion into the diamond anvils), as quasi-hydrostatic media in studying magnetic, superconducting, and structural properties in the megabar range.

4. Conclusions

In summary, one can assume that, in addition to the equalization of elastic characteristics of the materials of various classes, a new phenomenon should occur in the megabar pressure range— inversion of shear rigidity. Molecular substances such as rare-gas solids may surpass metals, as well as the ionic and covalent materials, in shear modulus and hardness. Such relative behaviour of the moduli should be taken into account when analysing various processes in the interior of the Earth and planets and also in high-pressure (megabar-range) experimental techniques. Clearly, the predicted phenomenon has a transient character. After the metallization of ionic and molecular materials at pressures of 1–10³ Mbar, the elastic moduli of all substances will be determined only by the corresponding atomic numbers.

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