

# Description of non-linear elasticity valid up to extremely large hydrostatic stresses

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## 1. Introduction

Under purely hydrostatic loading conditions irreversible deformations of materials by plastic shear are excluded, i. e. solids behave in an elastic manner up to extremely large stresses and strains, resp.. Consequently, for non-infinitesimal strains, nonlinearly elastic relations between stress and strain exist, which partly have been described on the basis of lattice theories (see, e. g. [1 - 3]), second-order theories of elasticity (also approaches to a third order theory) [4 - 9], and empirical relations, resp., gained from experimental compression data (compare the survey on literature given in [9 - 12]).

Bridgman [13], [14] carried out high-pressure experiments over several decades of years and he was the first to give a relation between volume change and pressure as well as valuable data on material constants, characterizing the non-linearly elastic behaviour solids. Later, in the framework of a second-order theory mentioned, these constants were used for determining the so-called modulus of third order,  $b_{K0}$  (compare, e. g. [15]).

At present, due to rapid developments in high-pressure physics and geophysics, resp., a comparatively extensive set of compression data are available for many materials. Data on the bulk modulus  $K_0$  and on the modulus  $b_{K0}$  (also described by  $\kappa_0$  and  $\kappa_1$ , resp.) are compiled in [7], [9] and [15], e. g.. Furthermore, attempts were made to extend the range of validity of second-order theories. Ullmann and Pankov [9] (see also [10 - 12]) and other authors, too (see e. g. Somerville and Thomsen [16]), tried to estimate the modulus of fourth order,  $\kappa_2$ , and the authors of the paper [9] developed a mathematical model for a uniform description of compression data, valid up to about 50 (or more) per cent of volume change.

In the present paper a relation between volume ratio  $V/V_0$  and stress will be formulated, apparently valid up to extremely large stresses. The original purpose of this study was the determination of changes in the modulus in dependence on hydrostatic strains and of maximum cohesive stresses of solids, respectively. Thus, the range of validity of known second-order theories has been tested, which then led to the extension described here. Preliminary results were reported on in the papers [17 - 20]. Some of the equations described in [20] have been quoted again in this paper. For the sake of some comparisons results based on second-order theories are being represented in the following section.

## 2. Relations based on second-order theories

The elastic potential  $\Psi$  related to the initial volume  $V_0$  has been formulated by Murnaghan [4] (see also [5]) as a function of the Eulerian strain  $\epsilon$  (general loading condition):

$$\Psi = \left(\frac{\lambda}{2} + \mu\right) \epsilon_1^2 - 2\mu \epsilon_{II} + l' \epsilon_1^3 + m' \epsilon_1 \epsilon_{II} + n' \epsilon_{III}, \quad (1)$$

where respectively  $\epsilon_1$ ,  $\epsilon_{II}$ ,  $\epsilon_{III}$  are the first, second and third scalar invariants of the strain tensor (strain related to the deformed state), and  $\lambda$  and  $\mu$ , resp., are Lamé's elastic constants of second order, i. e.

$$\lambda + \frac{2}{3} \mu = K_0 \quad (2)$$

and

$$\mu = G_0 \quad (3)$$

( $K_0$  is the bulk modulus,  $G_0$  is the shear modulus). Furthermore,  $l'$ ,  $m'$  and  $n'$  are material constants of third order.

For hydrostatic conditions we have

$$\epsilon_1 = 3 \epsilon; \quad \epsilon_{II} = 3 \epsilon^2; \quad \epsilon_{III} = \epsilon^3. \quad (4)$$

Consequently, by means of eqs. (2) to (4), (1) appears as

$$\Psi = \frac{9}{2} K_0 \epsilon^2 + (27l' + 9m' + n') \epsilon^3. \quad (5)$$

The material constants of third order in eq. (5) are connected with

$$b_{K0} = \left. \frac{dK}{dp} \right|_{p \rightarrow 0} = - \left. \frac{dK}{d\sigma} \right|_{\sigma \rightarrow 0} \quad (6)$$

by

$$27l' + 9m' + n' = - \frac{9K_0}{2} (b_{K0} - 4) \quad (7)$$

(compare, e. g. [5] or [17]), where  $p$  and  $\sigma$ , resp., are the Eulerian pressure or stress, resp., and  $K$  is the 'momentary' bulk modulus defined by

$$K = V \frac{d\sigma}{dV} \quad (8)$$

so that  $K_0$  is given by

$$K_o = \left[ V \frac{d\sigma}{dV} \right]_{V \rightarrow V_o} \quad (9)$$

The relation between the hydrostatic stress  $\sigma$  and the strain  $\epsilon$  may be derived from (5), as  $\Psi$  is given by

$$\Psi = \frac{1}{V_o} \int_{V_o}^V \sigma dV. \quad (10)$$

Thus one gets  $\sigma$  from

$$\sigma = \frac{d\Psi}{dV/V_o} = \frac{d\Psi}{d\epsilon} \frac{d\epsilon}{dV/V_o} \quad (11)$$

The relation between  $\epsilon$  and  $V/V_o$  is described by

$$\frac{V}{V_o} = \frac{1}{(1-2\epsilon)^{3/2}} \text{ or, } \epsilon = \frac{1}{2} \left( 1 - \left( \frac{V_o}{V} \right)^{2/3} \right) \quad (12)$$

which, for our purpose, may be represented by a series expansion. After derivation and multiplication (see, e. g. [17]) equation (11) yields<sup>1)</sup>

$$\sigma = 3 K_o \left[ \epsilon - \epsilon^2 \left( \frac{3}{2} b_{KO} - 1 \right) \right], \quad (13)$$

if  $\epsilon$  terms of higher than second order are neglected. By means of (12), eq. (13) may be expressed as a function of volume ratio  $V/V_o$ :

$$\sigma = 3 K_o \left\{ \frac{3}{4} - \frac{3}{8} b_{KO} + \left( \frac{V_o}{V} \right)^{2/3} \left[ \frac{3}{4} b_{KO} - 1 \right] - \left( \frac{V_o}{V} \right)^{4/3} \left[ \frac{3}{8} b_{KO} - \frac{1}{4} \right] \right\} \quad (14)$$

Furthermore, the momentary bulk modulus  $K$  and its derivative with respect to the pressure, i. e.

$$b_K = \frac{dK}{dp} \quad (15)$$

are easily obtained from eqs. (8) and (14), i. e.

$$K = K_o \left\{ \left[ \frac{3}{2} b_{KO} - 1 \right] \left( \frac{V_o}{V} \right)^{4/3} - \left[ \frac{3}{2} b_{KO} - 2 \right] \left( \frac{V_o}{V} \right)^{2/3} \right\} \quad (16)$$

and, by means of (15) and (16), taking into account

$$\frac{dK}{dp} = - \frac{dK}{dV/V_o} \left( \frac{d\sigma}{dV/V_o} \right)^{-1} \quad (17)$$

one obtains

1) Of course, eq. (13) may also be derived from Murnaghan's tensor relation between stress and strain (see also [5] or [17]).

$$b_K = \frac{4}{3} \left\{ \frac{\left[ \frac{3}{2} b_{KO} - 1 \right] - \left[ \frac{3}{4} b_{KO} - 1 \right] \left( \frac{V_o}{V} \right)^{2/3}}{\left[ \frac{3}{2} b_{KO} - 1 \right] - 2 \left[ \frac{3}{4} b_{KO} - 1 \right] \left( \frac{V_o}{V} \right)^{2/3}} \right\} \quad (18a)$$

or

$$b_K = \frac{4}{3} \left\{ 1 + \left[ 2 \frac{[b_{KO} - 2/3]}{[b_{KO} - 4/3]} \left( \frac{V_o}{V} \right)^{2/3} - 2 \right]^{-1} \right\} \quad (18b)$$

after some rearrangements.

Equations (14), (16) and (18) yield the following data for special conditions:

For  $\frac{V}{V_o} \rightarrow 0$ :

$$\begin{aligned} \sigma &\rightarrow -\infty \\ \frac{K}{K_o} &\rightarrow \infty \\ b_K &\rightarrow 4/3. \end{aligned} \quad (19)$$

For  $\frac{V}{V_o} \rightarrow 1$ , necessarily:

$$\begin{aligned} \sigma &\rightarrow 0 \\ K &\rightarrow K_o \\ b_K &\rightarrow b_{KO}, \end{aligned} \quad (20)$$

$$\text{and for } \frac{V}{V_o} \rightarrow \left( \frac{\frac{3}{2} b_{KO} - 1}{\frac{3}{2} b_{KO} - 2} \right)^{3/2} = \frac{V_m}{V_o} :$$

$$\begin{aligned} \sigma &\rightarrow \sigma_m = \frac{K_o}{2 b_{KO} - 4/3} \\ \frac{K}{K_o} &\rightarrow 0 \\ b_K &\rightarrow \infty, \end{aligned} \quad (21)$$

where  $\frac{V_m}{V_o}$  and  $\sigma_m$ , resp., are the maximum values of volume ratio and tensile stress (maximum cohesion stress) of solids.

An alternative representation, on the basis of a second-order theory, was developed by Pfleiderer, Seeger and Kroener [5], according to which the elastic potential related to the initial volume as a function of stress is given by (general case):

$$\Omega = \frac{\sigma_I^2}{2 E_o} - \frac{\sigma_{II}}{2 G_o} + L \sigma_I^3 + M \sigma_I \sigma_{II} + N \sigma_{III}, \quad (22)$$

where  $\sigma_I$ ,  $\sigma_{II}$ ,  $\sigma_{III}$  are the first, second and third scalar invariants of the stress tensor, resp., and  $L$ ,  $M$ ,  $N$  are ma-

terial constants of third order. For hydrostatic conditions, (22) reduces itself to

$$\Omega = \frac{\sigma^2}{2K_0} + \frac{\sigma^3}{6K_0^2} (b_{K0} + 4) \quad (23)$$

as

$$3K^2 (27L + 9M + N) + \frac{1}{9K} (27l' + 9m' + n') = 4 \quad (24)$$

(see [5]) and furthermore, as the scalar invariants of the stress tensor correspond to the relations given in (4), if  $\sigma$  instead of  $\epsilon$  is introduced there.

The second-order relation between volume change and hydrostatic stress is represented by (see, e. g., [15] or [17]).

$$\frac{V - V_0}{V_0} = \frac{\sigma}{K_0} + \frac{\sigma^2}{2K_0^2} (b_{K0} + 1). \quad (25)$$

Compared with Murnaghan's relations, i. e. eqs. (5) or (14), resp., equations (23) and (25) have a much smaller range of validity as will be shown in the fourth section. Nevertheless, they proved to be useful in treating special problems [5].

Besides, other second-order representations have been formulated on the basis of the Lagrangean strain (see [8] and a survey in [7], where also Birch's and Brugger's notations for the higher order constants are described), but there are similar restrictions with respect to the range of validity if compared with Murnaghan's formulation. The relation between the Lagrangean strain  $\epsilon_A$  and the volume ratio  $V/V_0$  is given by (hydrostatic conditions):

$$\epsilon_A = \frac{1}{2} \left( \left( \frac{V}{V_0} \right)^{2/3} - 1 \right) \quad (26)$$

### 3. Non-linear relations with a wide range of validity<sup>3)</sup>

A general material law for hydrostatic loading conditions can be obtained by rearranging eq. (8),

$$\frac{dV}{K} = \frac{d\sigma}{K}, \quad (27)$$

and by integrating (27), which yields

$$\frac{V}{V_0} = \exp \left\{ \int_0^\sigma \frac{d\sigma^*}{K} \right\}. \quad (28)$$

A Mc Laurin expansion of (28) leads to

- 2) This relation was given in a wrong way in [17] and has correspondingly to be replaced by (26).
- 3) In this section the author largely follows the representation given in section 2 of the paper [20].

$$\frac{V - V_0}{V_0} = \frac{\sigma}{K_0} + \frac{\sigma^2}{2K_0^2} (b_{K0} + 1) + R(\sigma) \quad (29)$$

where  $R(\sigma)$  is the remainder of the series with higher orders of  $\sigma$  and of the corresponding derivatives of  $K$  with respect to  $p$  at  $p \rightarrow 0$ , resp. Equation (29) is, of course, in agreement with the corresponding second-order relation (eq. (25)), if  $R(\sigma)$  is neglected.

On the presupposition that the function

$$K = f(\sigma) \quad (30)$$

is known, equation (28) represents the complete non-linear material law of arbitrarily high order. Therefore, an attempt was made on the basis of trial and error to find this function. The following conditions, which have to be fulfilled by such an expression, were set:

- { 1 } : There exists a maximum tensile stress  $\sigma_m^+$  (maximum cohesion stress of solids) so that

$$\frac{d\sigma}{dV} \Big|_{V \rightarrow V_m^+} \rightarrow 0 \text{ or } K \Big|_{V \rightarrow V_m^+} \rightarrow 0 \text{ (see eq. (8))} \quad (31)$$

The numerical value of  $\sigma_m^+$  has to agree with the „most reliable” values of  $\sigma_m^+$  computed on the basis of lattice theories.

- { 2 } : For  $\sigma \rightarrow -\infty$ , we expect  $V \rightarrow 0$  and  $K \rightarrow \infty$

- { 3 } : With  $f(\sigma)$  being introduced, the second-order approximation of eq. (28) has to agree with (25).

- { 4 } : All known experimental data and „physically reasonable” arguments, resp., (additionally introduced to those considered above) have to be reproduced in the range of  $-\infty \leq \sigma \leq \sigma_m^+$  for different types of materials.

Condition { 4 } is restricted this way that static compression data have to be reproduced, and furthermore that phase transitions are neglected.

Fortunately, the conditions { 1 } and { 4 } have implied such strong restrictions that all but one function out of a large number of others could be rejected. This function, at least at a high degree of accuracy, is

$$\frac{K}{K_0} = \frac{-\sigma/\sigma_m^+}{\ln(1 - \sigma/\sigma_m^+)} \quad (32)$$

where

$$\sigma_m^+ = \frac{K_0}{2b_{K0}} \quad (33)$$

is identical with the maximum cohesion stress of solids (see below). Thus, inserting (32) in (28) and using (33), the material law appears as

$$\frac{V}{V_0} = \exp \left\{ -\frac{1}{2b_{K0}} \int_0^\sigma \frac{\ln(1 - \sigma^*/\sigma_m^+)}{\sigma^*} d\sigma^* \right\} \quad (34)$$

The integral is the Dilogarithm function

$$-\int_0^{\sigma} \frac{\ln(1 - \sigma^*/\sigma_m^+)}{\sigma^*} d\sigma^* = \sum_{\nu=1}^{\infty} \frac{(\sigma/\sigma_m^+)^{\nu}}{\nu^2} \quad (35)$$

but the series representation is only valid for  $|\sigma/\sigma_m^+| \leq 1$  (see e. g. [21]). In general, the integral has to be computed numerically. Some data will be given in the appendix of this paper. For extremely high pressures ( $p \geq 100 \sigma_m^+ \approx 10 K_o$ , i. e.  $p \geq (10^5 \dots 10^6)$  MPa for many materials) eq. (34) reduces itself to

$$\frac{V}{V_o} = \exp \left\{ -\frac{1}{2b_{KO}} \left\langle \frac{1}{2} [\ln(p/\sigma_m^+)]^2 + \frac{\pi^2}{6} \right\rangle \right\} \quad (36)$$

Before giving remarks on the validity of the material law we shall add some other expressions characterizing the mechanical behaviour of solids.

The 'momentary' material constants  $b_K = \frac{dK}{dp}$  and  $\frac{d^2K}{dp^2}$  are derived from (32):

$$b_K = 2b_{KO} \left\{ \frac{1}{\ln(1+p/\sigma_m^+)} - \frac{p/\sigma_m^+}{\ln(1+p/\sigma_m^+)^2 (1+p/\sigma_m^+)} \right\} \quad (37)$$

$$\frac{d^2K}{dp^2} = \frac{4b_{KO}^2}{K_o}$$

$$\left\{ \frac{-2(1+P/\sigma_m^+) \ln(1+P/\sigma_m^+) + (P/\sigma_m^+) [2 + \ln(1+P/\sigma_m^+)]}{(1+P/\sigma_m^+)^2 [\ln(1+P/\sigma_m^+)]^3} \right\} \quad (38)$$

Being subsequently derived with respect to  $p = -\sigma$  constants of arbitrarily high order may be obtained, but in the frame of our representation only two parameters,  $b_{KO}$  and  $K_o$ , are required, i. e. constants of fourth and higher order are not necessary. Finally, the strain energy density for hydrostatic conditions (see (10)) is

$$\Omega = \frac{1}{V_o} \int_0^V \sigma dV \quad (39)$$

After  $dV$  has been substituted, which is easily derived from (32) or (34), eq. (39) appears as

$$\Omega = -\frac{\sigma_m^+}{2b_{KO}} \int_0^{\sigma} \ln(1 - \sigma^*/\sigma_m^+) d\sigma^* \left[ \exp \left\{ -\frac{1}{2b_{KO}} \int_0^{\sigma^*} \frac{\ln(1 - \sigma^*/\sigma_m^+)}{\sigma^*} d\sigma^* \right\} \right] \frac{d\sigma^*}{\sigma_m^+} \quad (40)$$

If in eq. (40) the pressure,  $p = -\sigma$ , is introduced instead of  $\sigma$ , the sign in front of the first integral on the right side becomes positive.

#### 4. Check of validity, comparison and representation, resp., of the results

At first it has to be shown that within the restrictions mentioned the conditions {1} to {4} are fulfilled.

{1} : For  $\sigma \rightarrow \sigma_m^+$  the limiting value of  $K$  (see eq. (32)) is zero as required. Values of  $\sigma_m^+$  used for comparison should be most reliable if computed on the basis of the Born-Mayer lattice theory. The good agreement between these data and values obtained by means of eq. (33) has been shown in [19] (see also [22]). The corresponding value of the volume ratio  $V/V_o$  for  $\sigma/\sigma_m^+ \rightarrow 1$  results from (34) and (35)

$$\frac{V_m^+}{V_o} = \exp \left\{ \frac{\pi^2}{12b_{KO}} \right\} \quad (41)$$

as the limiting value of the Dilogarithm series is  $\frac{\pi^2}{6}$  for  $\sigma/\sigma_m^+ \rightarrow 1$ .

{2} : By means of (36) the result of  $V \rightarrow 0$  for  $p \rightarrow \infty$  is obvious.

{3} : If in eq. (34) the integral is substituted by the infinite series (eq. (35)) and if then the well-known series

$$e^x = 1 + x + \frac{x^2}{2!} + \dots$$

is reduced to the second-order approximation, where the same is done with

$$x = \frac{1}{2b_{KO}} \sum_{\nu=1}^{\infty} \frac{(\sigma/\sigma_m^+)^{\nu}}{\nu^2}$$

one verifies eq. (29) for  $R(\sigma) \rightarrow 0$  (or (25), resp.). At the same time, this means that  $b_K \rightarrow b_{KO}$  and  $K \rightarrow K_o$ , resp., if  $\sigma \rightarrow 0$ , which is easily obtained by corresponding derivations or on the basis of eqs. (37) and (32) for  $\sigma \rightarrow 0$ .

{4} : Data computed on the basis of the material law (eq. (34)) almost completely match the path of experimental compression data (static compression) available up to pressures of about  $10^2$  GPa for metals, ionic and molecular materials, resp.. Comparative examples of more than 30 solids were given in [19] and [20]. The maximum pressures reached correspond to  $p \approx (1 \dots 10) K_o$  for many materials, whereas the respective volume ratios are about  $V/V_o \approx 0,4$ . A good agreement was also shown [20] to exist with „interpolated” data for H, H<sub>2</sub>O and Ar given by Zharkov et al. [23]. These data are due to the interpolation of experimental and quantum-statistical values, resp., for pressures up to about  $10^3$  GPa.

There are other hints giving rise to believe in a wide validity of the non-linear relations:

Apparently, as mentioned in [20], the relation (36) reveals the same dependence of the pressure  $p$  on the volume ratio  $V/V_0$  as the quantum statistical one in the case of highly degenerated matter, if  $p$  reaches a „critical” value  $p \rightarrow -\sigma_m^-$  inducing a volume collapse of matter. Reasonable data on such critical values have been obtained as will be shown in a subsequent paper.

Furthermore, after some rearrangements, the material law (eq. (34)), may be interpreted as a relation between entropies, i. e. entropies of „arrangement”, „excitation” and „cohesion”, resp., as defined in [20] with the result that the entropy of arrangement always reaches an extreme, after the excitation (i. e. the entropy of excitation) has been changed by increasing the stresses. Details are described in [20]. There it has also been shown, that the characteristic constants of the solid state are the stresses at the upper and lower existence limit of solids, i. e.  $K_0$  and  $b_{K0}$  appear as derived quantities.

Now some relations will be represented graphically. Fig. 1 shows the dependency of the volume on the stress according to eq. (34), given here as the plot  $\sigma/\sigma_m^+$  over  $\Delta V/V_0 = (V - V_0)/V_0$ . The influence of the parameter  $b_{K0}$ , the modulus of third order, can be seen, which amounts to  $3 \leq b_{K0} \leq 7$  for many materials. (Note that  $\sigma_m^+ = K_0/2b_{K0}$  used in the dimensionless ratio  $\sigma/\sigma_m^+$  depends on  $b_{K0}$ ). For  $\sigma/\sigma_m^+ \rightarrow 1$  the curves always show a horizontal tangent, which in Fig. 1, however, lacks in clearness, as the curvature of the curves changes rapidly in the very vicinity of  $\sigma/\sigma_m^+ \rightarrow 1$ , as demonstrated in the next figure (Fig. 2), in which  $K = V d\sigma/dV$ , the momentary bulk modulus (according to eq. (32)), is plotted over  $\sigma/\sigma_m^+$ : There is a steep decay of  $K$  to zero very close to  $\sigma/\sigma_m^+ \rightarrow 1$ . Equally, the variation of  $K$  with stress is demonstrated up to very high pressures. The usual assumption that  $K$ , approximately, changes proportionally to the stress is only justified within suitably small intervals, but the intervals may be chosen the larger the higher the pressures are. This is also shown in Fig. 3, where the derivative of  $K$  with respect

to  $\sigma$ , i. e.  $b_K = -\frac{dK}{d\sigma} = \frac{dK}{dp}$  is plotted over  $\sigma/\sigma_m^+$  (eq. 37)). Figs. 2 and 3 may be used to demonstrate the modulus changes of prestressed solids, if a certain point in the curves, marked by a certain prestress, is considered the new reference state.

Finally, the elastic potential (eq. (40)) related to the initial volume  $V_0$  is represented in Fig. 4, here in dependence on  $r/r_0 = (V/V_0)^{1/3}$ , which is the usual plot for potentials formulated on the basis of lattice theories. The full circles mark data corresponding to the Born-Mayer potential, but this will be described in another paper, i. e. it will be omitted here.

Some comparisons with the second-order approximation by Murnaghan are added:

In Fig. 2 values of  $K$  due to the second-order relation (16) for two different parameters ( $b_{K0} = 4$  and 6, resp.), may be compared with our results (eq. (32)) which, in this plot over  $\sigma/\sigma_m^+$ , yield only one curve for

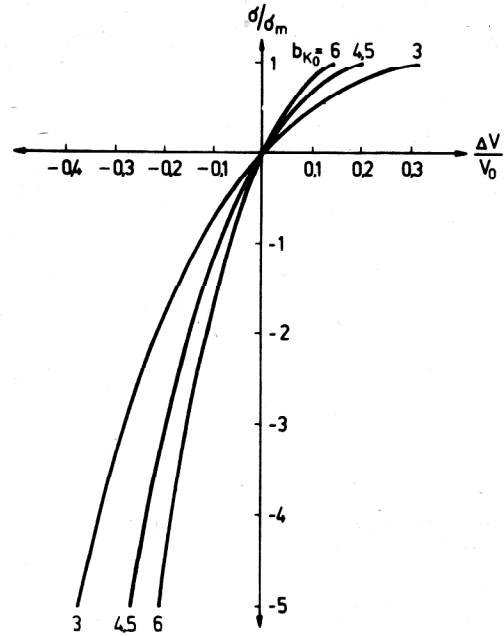


Fig. 1  
Dependence of dimensionless stress  $\sigma/\sigma_m^+$  on volume change  $\Delta V/V_0 = (V - V_0)/V_0$  according to eq. (34).

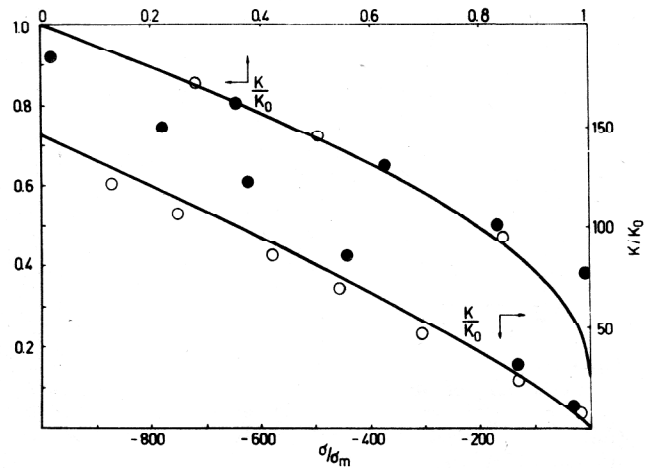
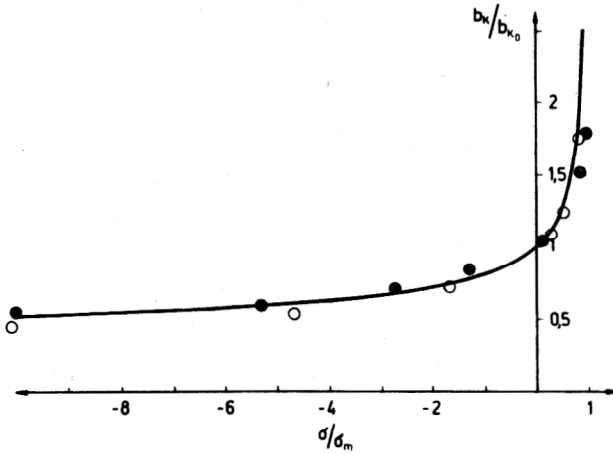


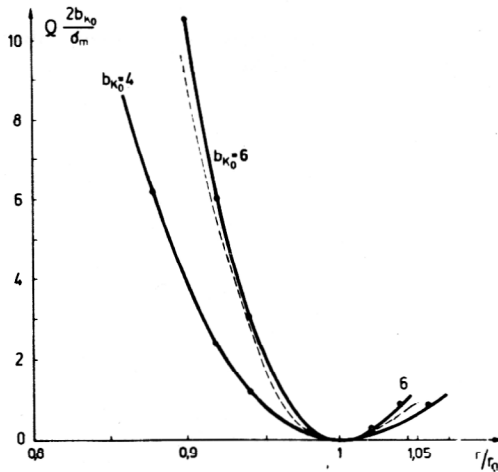
Fig. 2  
Variation of momentary bulk modulus  $K$  over  $K_0$  with dimensionless stress  $\sigma/\sigma_m^+$  (curves) according to eq. (32). Points mark data due to the second-order relation (16) for  $b_{K0} = 4$  (full circles) and  $b_{K0} = 6$  (open circles). The upper curve is related to the co-ordinates marked at the left and upper border of this figure, whereas the lower curve is related to the co-ordinates at the right and lower border, respectively.

arbitrary values of  $b_{K0}$ . (Note that the influence of the parameters  $b_{K0}$  on the  $K/K_0$  values for given stresses  $\sigma$  affects our relation (32) by  $\sigma_m^+ = K_0/2b_{K0}$ ).

Deviations of the second-order representation are noticed to increase considerably at relatively large stresses, but in a different way for different  $b_{K0}$  values. In Fig. 3  $b_K$  data computed on the basis of eq. (18) (for  $b_{K0} = 4$  and 6, resp.) may be compared with our results, where again the plot of Fig. 3 over  $\sigma/\sigma_m^+$  according to eq. (37) yields only one curve for arbitrary  $b_{K0}$  values. Deviations are relatively large, if  $\sigma/\sigma_m^+$  approaches the limiting value 1 (see the text below). Besides, the  $b_K$  values differ noticeably for very high pressures as can be derived from Fig. 2.



**Fig. 3**  
Variation of momentary modulus of third order  $b_K$  over  $b_{K0}$  with dimensionless stress  $\sigma/\sigma_m^+$  (curves) according to eq. (37). Points mark data due to the second-order relation (18) for  $b_{K0} = 4$  (full circles) and  $b_{K0} = 6$  (open circles), resp.. Note the relatively small range of stresses (compared with Fig. 2).



**Fig. 4**  
Representation of dimensionless strain-energy density over  $r/r_0 = (V/V_0)^{1/3}$  according to relations (40) and (34), resp. (full lines). Dashed curve corresponds to the second-order relation (5) for  $b_{K0} = 6$ . Details, see text.

For  $V \rightarrow 0$  ( $\sigma \rightarrow -\infty$ ) the second-order relation yields  $b_K \rightarrow 4/3$  (compare (19)), whereas the limiting value according to eq. (37) is zero.

Comparing the stress-volume relations (eqs. (14) and (34), resp.) one will see again that the deviations depend on both the stress level and the  $b_{K0}$  values in a complicated manner. For pressure ratios of  $p/\sigma_m^+ \leq 10$  deviations of the corresponding volume ratios are usually smaller than about  $\pm 5$  per cent, but for  $p/\sigma_m^+ \geq 100$  they become larger or much larger, resp. than 10 per cent. On the tensile side, the deviations are in the order of 10 per cent if  $\sigma/\sigma_m^+ \rightarrow 1$ , i. e. the second-order relations yield larger values (compare data according to (21) with the values given in (33) and (41), resp.)

Furthermore, the second-order approximation by Pfliderer, Seeger and Kroener [5] for the volume change in dependence on the stress (eq. (25)) was compared with our representation (eq. (34)). One will easily conclude that the approximation can be used for stresses

$$|\sigma| \leq \frac{K_0}{4 b_{K0}}$$

The deviations of the volume changes will then be smaller than about four per cent. For larger stresses the approximation completely fails (see, e. g. the comparison made in Fig. 1 of the paper [19]).

The volume-stress relation may also be compared with the approach by Ullmann and Pankow [9]. The agreement partly depends on the accuracy of the values they obtained for the modulus of fourth order (see [11], [12]), given by

$$\kappa_2 = K_0 \left. \frac{d^2 K}{dp^2} \right|_{p \rightarrow 0} \approx \frac{1}{9} (1 + b_{K0}) (1 - 2 b_{K0}). \quad (42)$$

The  $\kappa_2$  values of Ullmann and Pankow were mentioned [20] to correspond only roughly to ours, which are given by

$$\kappa_2 = -2/3 b_{K0}^2 \quad (43)$$

(following from (38) for  $p \rightarrow 0$ ), i. e. noticeable deviations in the range of about  $\frac{V}{V_0} \leq 0.5$  have been observed.

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#### Appendix

Numerical data for the volume ratio  $V/V_0$  in dependence on the stress ratio  $\sigma/\sigma_m^+$  for  $b_{K0} = 5$ .

The data given here may also be used for other values of  $b_{K0}^*$ , as (compare (34)) the relation

$$\frac{V^*}{V_0} = \left( \frac{V}{V_0} \right)^{b_{K0}^*}$$

holds for a given value of  $\sigma/\sigma_m^+$  ( $\frac{V^*}{V_0}$  is the volume ratio related to the value  $b_{K0}^*$ , whereas  $V/V_0$  is the ratio related to  $b_{K0} = 5$ , where both the ratios are related to the same value of  $\sigma/\sigma_m^+$ ). Values for the Dilogarithm function may also be used from (21) or computed numerically as done here. For ratios  $p/\sigma_m^+ > 100$  data may be obtained on the basis of (36).<sup>5)</sup>

4) Besides, from (14) to (18)  $\kappa_2 = -(b_{K0} - 2/3)(b_{K0} - 4/3)$  results.

5) Compared with the data of the table, eq. (36) yields  $V/V_0$  values which are smaller by about 1, 0.1 and 0.04 per cent, resp., for  $p/\sigma_m^+$  values of 10, 100 and 200, resp.

$\sigma/\sigma_m^+$	$V/V_0$	$\sigma/\sigma_m^+$	$V/V_0$
1	1.1788	- 12	0.6280
0.8	1.1135	- 14	0.6030
0.6	1.0755	- 16	0.5811
0.4	1.0459	- 18	0.5617
0.2	1.0213	- 20	0.5442
- 0.25	0.9767	- 25	0.5073
- 0.5	0.9561	- 30	0.4772
- 0.75	0.9377	- 35	0.4521
- 1	0.9210	- 40	0.4306
- 2	0.8661	- 45	0.4119
- 3	0.8236	- 50	0.3954
- 4	0.7889	- 60	0.3675
- 5	0.7595	- 70	0.3445
- 6	0.7341	- 80	0.3251
- 8	0.6916	- 90	0.3085
- 10	0.6571	- 100	0.2940

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