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Application of High Precision Band Structure Calculations to the Equation of State for Beryllium Oxide: SESAME Equation of State Number 7612

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APPLICATION OF HIGH PRECISION BAND STRUCTURE CALCULATIONS TO THE EQUATION OF STATE FOR BERYLLIUM OXIDE:
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by

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ABSTRACT

High precision electronic band structure calculations for BeO have revealed a large volume discontinuity structural phase transition on the 0 K isotherm at about 1 Mbar. Although, this transition has not been observed experimentally, the accuracy of the calculations is such that the existence of this transition is unambiguous. A transition of this magnitude is likely to have a substantial impact on hydrodynamic simulations involving BeO. Here we report the creation of a new SESAME equation of state for BeO which incorporates the effect of the theoretically determined phase transition. This new EOS will be added to the SESAME library as material number 7612.

Beryllium oxide (BeO) is of great interest to scientists for diverse reasons. First, there is a basic interest in BeO due to its unique position as the lightest of the II-VI compounds (a very important class of compounds in general). BeO is also of considerable interest to material scientists because of its basic properties (high thermal conductivity, low electrical conductivity, piezoelectric properties, light ceramic, etc.). In addition, BeO is of great technological importance as a moderator in nuclear reactors. For these reasons, BeO has been of recurring interest to SESAME equation of state (EOS) library users, and it is important that the EOS for BeO should be revised as new data becomes available.

Existing BeO EOS's in the library have been called into question by recent theoretical evidence for a large volume discontinuity phase transition at high pressures from the ambient wurtzite (B4) structure to the more dense rocksalt (B1) phase.[1-3] Two separate investigations have predicted such a transition but have disagreed as to the calculated transition pressure (217 kbar using the pseudopotential method[2] and about 400 kbar using the potential induced breathing method[3]). In an attempt to resolve this discrepancy, we have performed a high precision first principles calculation of the 0 K isotherm for BeO using the full potential linear muffin-tin-orbitals (FLMTO) band structure method. (The FLMTO method is substantially more reliable than either of the methods used previously to study BeO.) In our investigation, we considered both the B4 and B1 phases, and slightly adjusted our final results to ensure that the ambient density is reproduced. (Details of our calculations will be published elsewhere.)

Figure 1 shows our calculated pressure vs. density curves ($0.9 < \rho/\rho_0 < 2.0$) for the individual phases and for that mixture of phases which minimizes the Gibbs free energy. (Figure 2 shows the pressure vs. density curve over the full range of densities treated in the FLMTO calculations.) It is apparant from Fig. 1 that the B4 → B1 phase transition occurs at about 940 kbar (±100 kbar) and involves a volume collapse of roughly 12%. Such a large volume change can be expected to have a significant effect on hydrodynamic simulations and should not be neglected. The full impact of this transition on simulations can be better judged by calculating the Hugoniot for BeO and comparing it with the experiment. However, such a Hugoniot calculation requires a complete SESAME EOS for BeO. Fortunately, the standard form for SESAME EOS's is such that it is straightforward to generate a global EOS which incorporates the new 0 K isotherm.

In the SESAME library, the EOS's are partitioned into three terms for the pressure P and the internal energy E:

$$P(\rho,T) = P_c(\rho) + P_n(\rho,T) + P_e(\rho,T) \qquad (1)$$

$$E(\rho,T) = E_c(\rho) + E_n(\rho,T) + E_e(\rho,T) \qquad (2)$$

where ρ is the density and T is the temperature. The subscripts c, n, and e denote the contributions due to the cold curve (zero temperature isotherm), the nuclear motion, and the thermal electronic excitations. It is thus possible to treat each term independently using any desired model. In the present case, we want to form a global EOS for BeO which incorporates our FLMTO results into the cold curve.

For our Hugoniot calculation, we first formed a new cold curve for BeO by using the general purpose SESAME EOS computor program GRIZZLY[4] to extend our 0 K isotherm into the expanded region by attaching a Lennard-Jones type tail,[4] and into the compressed region by smoothly switching over to a mixed Thomas Fermi Dirac (TFD) cold curve[4,5] at high compressions. A composite global EOS for BeO was then formed by using the nuclear and electronic thermal contributions from an already existing EOS for BeO (SESAME material number 7611[1]). The models used for those parts of the EOS were described in Ref. 1.

Figure 3. compares a U_s vs. U_p Hugoniot curve calculated from our composite BeO EOS (solid line) with experimental data.[6] (Note that in the mixed phase region the theoretical curve ignores two-wave effects and cannot be considered to have any real interpretation.) The theoretical curve is in good agreement with the experimental data for the range $1.2 < U_p < 3.0$ km/s and for the sound speed at $U_p = 0.0$. The remaining data is dominated by strength effects which are not considered in the theoretical curve. Thus, overall, the agreement with experiment is quite good for the composite EOS (solid line).

The large impact of the BeO phase transition on the Hugoniot is evident in Figure 3. Unfortunately, although the existence of the phase transition and its large impact are unambiguous, the detailed behavior of BeO in the mixed phase region is not entirely certain. First, it is possible that the predicted transition pressure could be off by as much as ±100 kbar. Even if the calculations were perfect, the actual transition under shock loading could be delayed due to metastability of the B4 phase beyond the equilibrium B4-B1 boundary. It is also likely that in the mixed phase region, the general shape of the real U_s vs. U_p curve could be dramatically different from that in Fig. 3. Examples of both of the latter phenomena have been observed in the quartz→stishovite phase transition in silica,[7] which is qualitatively similar to the B4→B1 transition in BeO.

In spite of the caveats just discussed, the new EOS for BeO should be more realistic than any of the existing EOS's in the SESAME library. However, rather than simply entering the EOS just discussed into the SESAME library, we have chosen to form still another cold curve for BeO which takes advantage of the experimental data in the B4 region of the phase diagram, uses the calculated 0 K isotherm for the high pressure B1 phase, and does not produce a two-wave structure in the mixed phase region. To accomplish this, we have constructed a hypothetical U_s vs. U_p Hugoniot for BeO which matches the experimental data in the low pressure region, matches the solid line in Fig. 3 for the high pressure region, and connects the two with a horizontal line in the mixed phase region. That hypothetical curve is shown in Figure 3 (dashed line) and can be represented by five (U_p,U_s) points: (0.0, 8.4), (2.94, 12.0), (4.68, 12.0), (6.4414, 14.4932), (8.78033, 17.5607), all in km/s.

Using the CHUG option in GRIZZLY, we have generated a new cold curve for BeO by removing thermal contributions from the Hugoniot defined by the dashed line in Fig. 3. That cold curve has then been combined with the nuclear and electronic thermal contributions taken from material number 7611 to form a new global EOS for BeO which will be added to the SESAME library as material number 7612. Figure 4 compares the cold curve for 7612 with that for 7611. Again, the enormous impact of the B4→B1 phase transition is obvious. Even at the highest pressures shown in Fig. 4 (about 15 Mbar), the new cold curve pressure is about 20% lower than that for 7611.

Although there are many unresolved questions about the actual behavior of BeO in and near the mixed phase region (0.8-2.0 Mbar), 7612 should be vastly superior to 7611 (and 7610) for $P > 2$ Mbar. Thus, 7612 should be the BeO EOS of choice for most problems. For applications which are dependent on the EOS of BeO in the mixed phase region, users should consider doing comparative runs using 7612 and 7610 to determine the impact of the EOS's on their results. We also encourage further experimental research on BeO in that range.

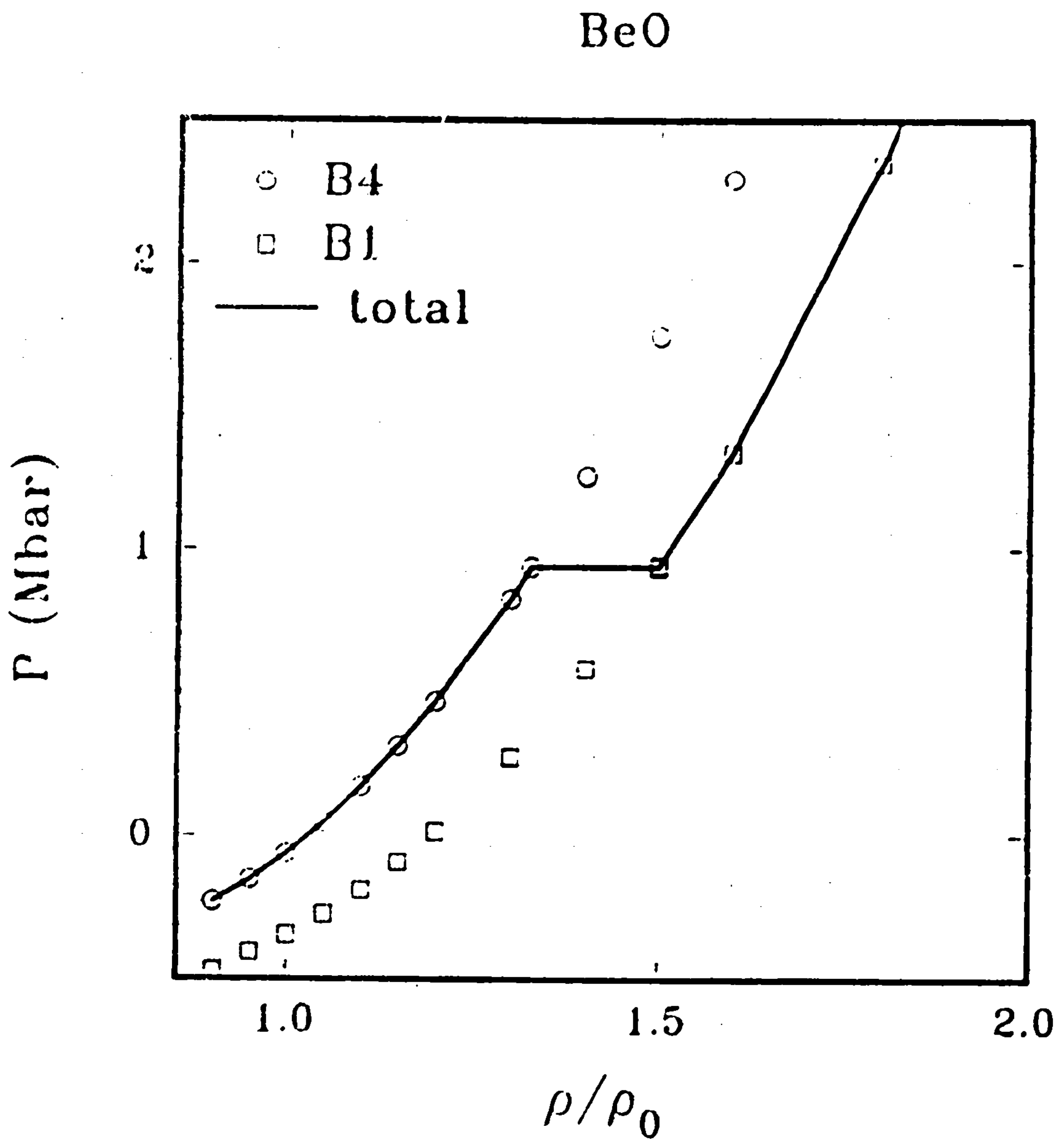

Figure 1 - The pressure vs. density points calculated via the FLMTO method for the B4 and B1 phases of BeO. The solid line is the 0 K isotherm which minimizes the Gibbs free energy.

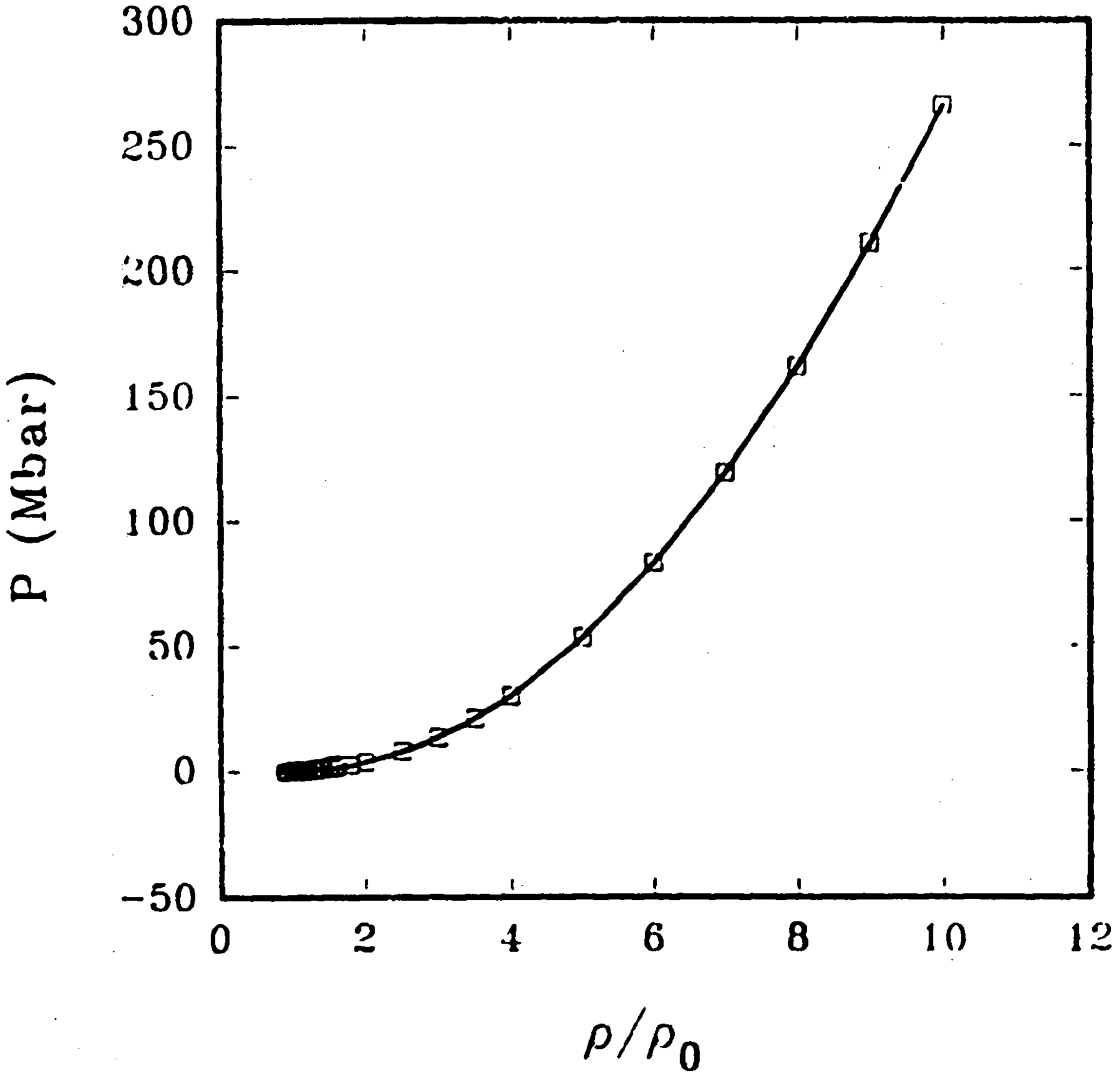

Figure 2 - Calculated 0 K isotherm for BeO obtained with FLMTO calculations.

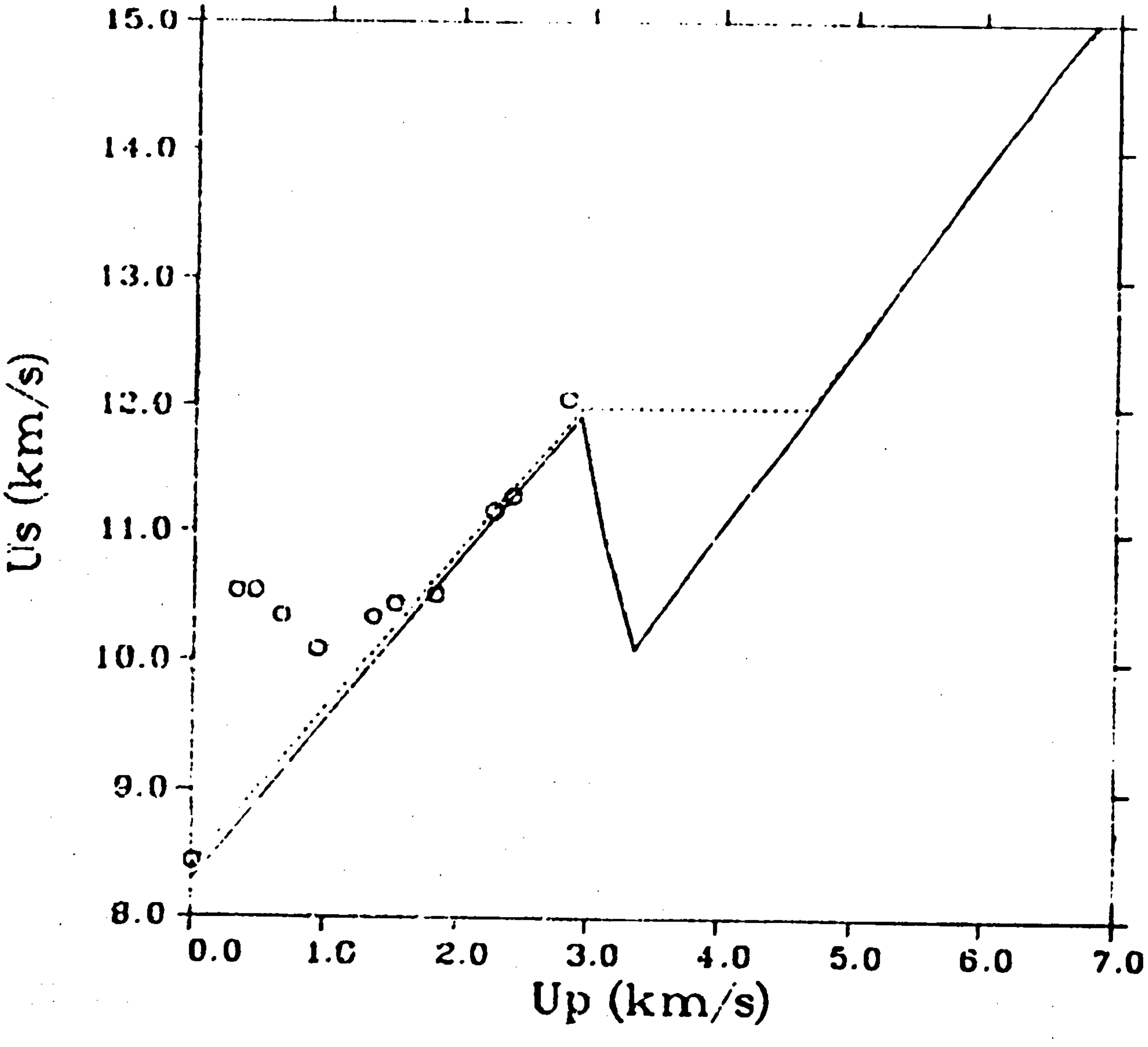

Figure 3 - The calculated principal Hugoniot for BeO (solid line) is compared to the experimental data of Ref. 6. Also shown is the straightline fit used in generating material number 7612 (dashed line).

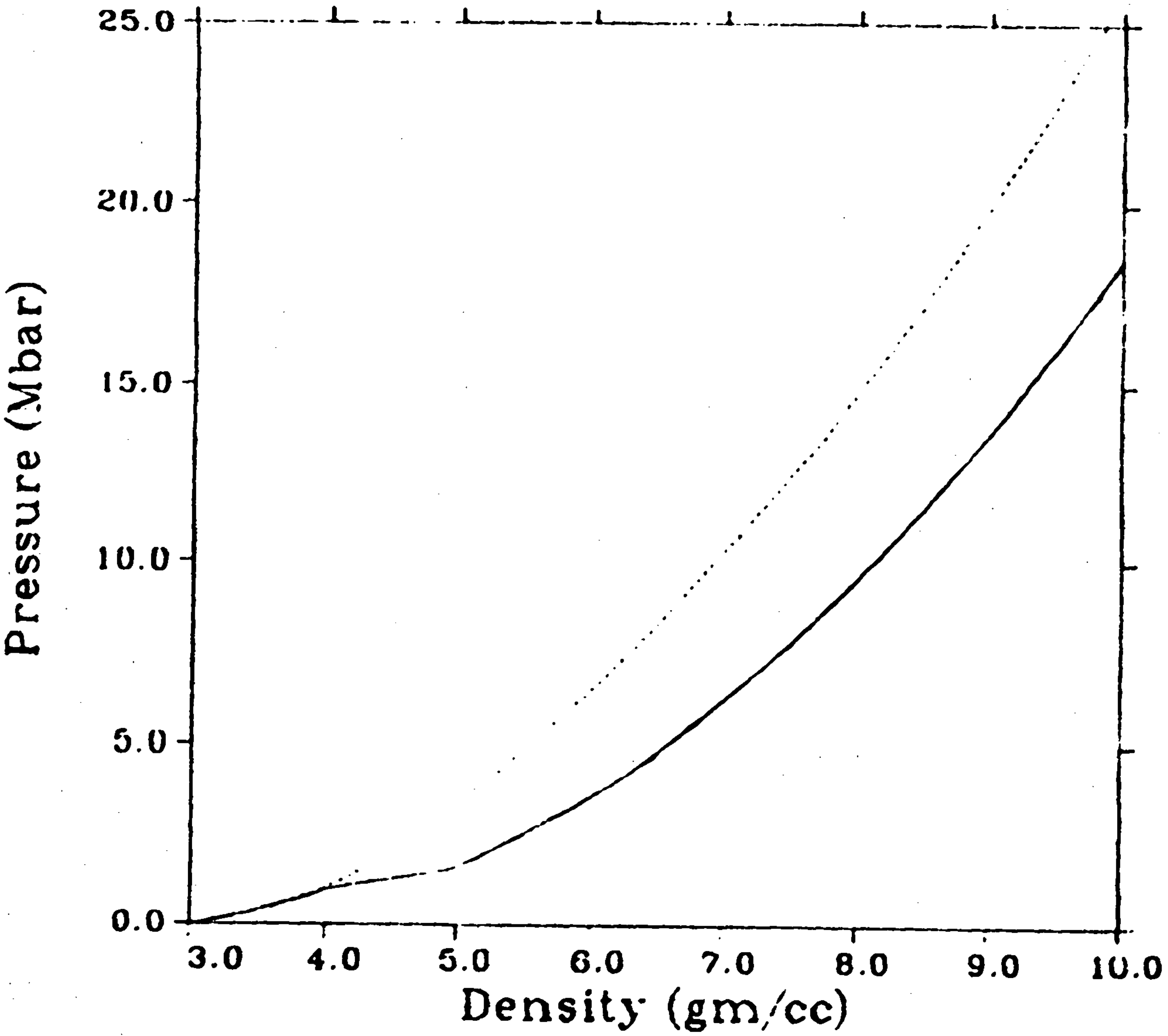

Figure 4 - Cold curves are shown for material numbers 7612 (solid line) and 7611 (dashed line).

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