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Comment on "Molybdenum sound velocity and shear modulus softening under shock compression"

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In this Comment we discuss recent results presented by Nguyen *et al.* on shock compressed molybdenum up to 438 GPa [Phys. Rev. B **89**, 174109 (2014)]. The aim of Nguyen's article is to show that there is no phase transition near 210 GPa. We propose instead an interpretation of their data that this material shows the onset of partial melting along the Hugoniot at 240(20) GPa, which is evident from abrupt changes in the pressure dependence of the shear modulus. This interpretation may solve the significant controversy in the melting slopes derived from shock and static experiments.

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Nguyen *et al.* [1] recently reported measurements of the longitudinal sound velocity in shock compressed molybdenum (Mo), along the Hugoniot up to 438 GPa. Based on their measurements, they concluded that "there is no statistically significant evidence for a previously reported bcc-hcp phase transition on the Hugoniot" of Mo, which was found near 210 GPa by Hixson *et al.* [2]. Nguyen *et al.* [1] also concluded that Mo remained in a stable bcc phase up to the shock melting pressure at 390 GPa. The purpose of this Comment is to show, from an examination of their sound velocity measurements and the shear modulus derived from them, that a different conclusion can be obtained from the experiments of Nguyen *et al.* [1]. Apparently, from their results it can be concluded that Mo softens above 240 GPa, which may be an indication of partial melting.

Plotted in Fig. 1 are the Mo sound velocities reported in Refs. [1,2]. In the figure it can be seen that both experiments show a clear discontinuity near 400 GPa. In addition, the experiments of Hixson *et al.* [2] have a discontinuity in the sound velocity at 210 GPa. The experiments of Nguyen *et al.* do not show this sharp discontinuity but clearly show a significant change in the pressure dependence of the sound velocity near 240 GPa as evident from a bilinear fit to their data. For $P < 240$ GPa the sound velocity (in kilometers per second) can be described by the linear function $C_{\mathrm{L}} = 7.12(5) + 0.0098(3)P$ (where P is in gigapascals). For $P > 240$ GPa the sound velocity can be represented by $C_{\mathrm{L}} = 8.94(4) + 0.0023(1)P$. The value of the high-pressure slope is 1/4 of the low-pressure slope. Both linear functions (see dashed lines in Fig. 1) intersect at 240(20) GPa. This pressure point and the one corresponding to the break reported by Hixson *et al.* [2] have a calculated temperature of ∼4100 K. These P-T conditions (240 GPa, 4100 K) agree with the extrapolation of a diamond-anvil cell (DAC) melting curve made up to 90 GPa and 3200 K [3,4]. The previous DAC melting measurements have been recently confirmed by novel sample-recovery experiments using electron microscopy techniques to identify melting [5].

Based on the previous experiments by Hixson *et al.* [2], there has been a considerable level of controversy in the literature on the character of the phase transition at 210 GPa. It has been assigned to melting [3,4], to a solid-solid transition [2,6], or a transition to a glasslike frustrated liquid [7]. Here we will show by employing the shear modulus calculated from the sound velocity measurements of Nguyen *et al.* [1] that there is indeed evidence for a structural change in Mo near 240(20) GPa (i.e., very close to 210 GPa previously reported [2]).

The shear modulus (G) is a magnitude very sensitive to structural changes. The shear modulus of Mo along the Hugoniot was calculated from the experimental longitudinal sound speed (C_{L}), bulk sound speed (C_{B}), and density (ρ), using the expression $G = \frac{3}{4}\rho(C_L^2 - C_B^2)$. The values for C_L and the density were taken from Ref. [1]. The values for the bulk sound speed were obtained from the work by Hixson *et al.* [2]. The calculated shear modulus of Mo is plotted in Fig. 2. In the figure we also include the shear modulus calculated using sound velocity measurements recently reported by Zhang *et al.* up to 162 GPa [8]. Results obtained from compressional and shear-wave measurements carried out in a large-volume press are also included [9].

In Fig. 2, it can be seen that starting from low pressure in the bcc solid phase, the values of G rise steeply to a peak value of ∼250 GPa near a pressure of 240 GPa. In particular, we found that all the data measured below 240 GPa can be well described by the analytic model proposed by Burakowsky *et al.* [10], assuming a shear modulus of 125 GPa at ambient conditions [9]. With increasing pressure above 240 GPa, G decreases from 250 GPa (at 240 GPa) to 160 GPa (at 380 GPa). Then G undergoes a collapse to a value of $G \sim 60(50)$ GPa near a pressure of 400 GPa.

The abrupt change in the pressure dependence of G at 240 GPa can be only explained by a transformation from bcc Mo to a different state of matter (named as Phase II in Fig. 2). The fact that the DAC melting curve [3] crosses the Hugoniot of Mo at the same P-T conditions (see Fig. 1 in Ref. [3]), suggests that Mo does not remain in the stable bcc phase above $210 - 240$ GPa (∼4100 K) but instead starts to melt with the values of the shear modulus decreasing to those of the liquid. This strong decrease in G with pressure beyond 240 GPa is significantly different from the behavior of a crystalline solid

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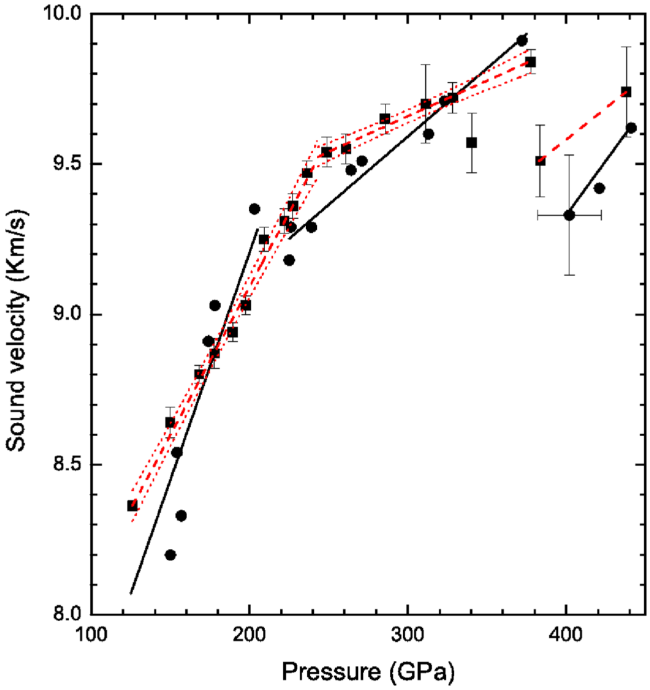

FIG. 1. (Color online) Pressure dependence of the sound velocity. Squares are from Ref. [1], and circles are from Ref. [2]. Solid lines are linear fits to the results of Hixson *et al.* [2], and dashed lines are linear fits to the results of Nguyen *et al.* [1] in different pressure ranges. The dotted lines indicate the 99% confidence level band of the fit to the results of Nguyen *et al.* [1].

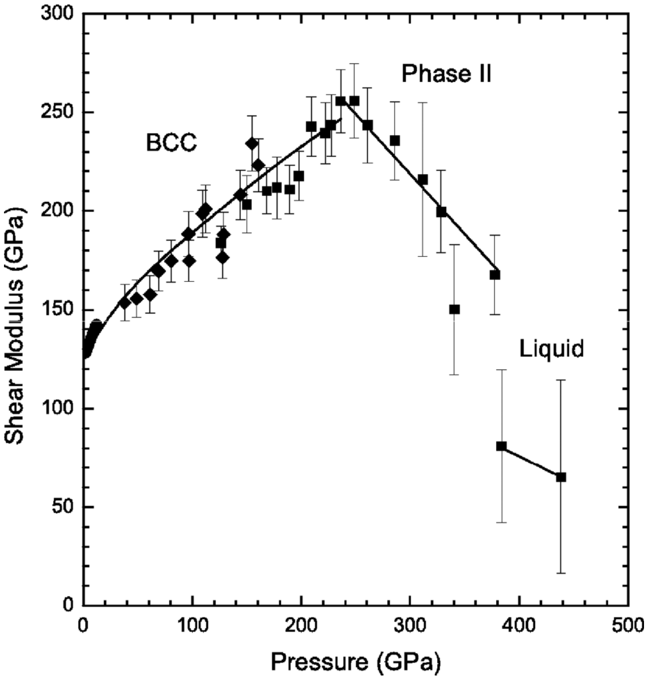

FIG. 2. Pressure dependence of shear modulus. The squares represent the values calculated from the data of Nguyen *et al.* [1]. Diamonds represent the shear modulus calculated from the data of Zhang *et al.* [8], and the circles represent the results reported by Liu *et al.* [9]. The solid line below 240 GPa is the shear modulus calculated using the model developed by Burakowsky *et al.* [10]. The solid lines above 240 GPa are a guide to the eye.

(see also Refs. [11] and [12]). Finally, above 380 GPa, after shock melting, the shear modulus is considerably smaller than at ambient pressure, but not zero, indicating that in the liquid phase Mo does not behave as a Newtonian fluid.

To summarize, we present evidence showing that in contrast with the statement made by Nguyen *et al.* [1], their sound velocity measurements provide evidence for a structural change in the Hugoniot of Mo near 210–240 GPa (~4100 K). Based on our calculated shear moduli, derived from the shock sound velocity data, we interpret this change to be the onset of partial melting. This would bring the shock data and the diamond cell melting data in agreement. We hope this Comment will trigger additional theoretical and experimental studies for a better understanding of the *P-T* phase diagrams of Mo and other transition metals and to accurately explore its melting curve and potential *HP-HT* polymorphism.

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