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$P(V)$ equations of state of solids: Density functional theory calculations and LDA versus GGA scaling

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We show that, by using a simple scaling of variables, the $P(V)$ equations of state calculated by the density functional theory (DFT) can be brought to a form which is essentially independent of the approximations used for the electronic exchange-correlation [local-density approximation (LDA), generalized gradient approximation (GGA)]. The respective predictions for $P(V)$ can thus be mapped onto each other and the comparisons experiment-theory focused on the details of $P(V)$ and its derivatives. It is argued that, as far as the $P(V)$ equation of state is concerned, the essential information provided by the DFT calculations is the pressure derivative of the bulk modulus—or the third volume derivative of the total energy E—which turns out, as well, to be nearly independent, in large range of volumes, of the choices made for the GGA or the LDA. The latter function of V, which represents the nonlinear elasticity under hydrostatic pressure, is consistently supplied by the DFT with much better accuracy than most of the experiments could presently provide. Implications for model descriptions of equations of state and for pressure calibration are discussed as well.

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I. INTRODUCTION

The equation of state (EOS) in the zero-temperature limit is the most fundamental characteristics describing the behavior of condensed matter at high pressures. Since realistic and accurate *ab initio* calculations on solids emerged in the early eighties, it became possible to obtain $P(V)$ from first principles; this approach provides the total energy $E(V)$ of which the $P(V)$ is the first derivative, $P(V)=-dE(V)/dV$, as well as all components σ_{ij} of stress. Knowledge of the variation in pressure P with volume V for a single phase determines the equilibrium volume V_0, and gives access to the bulk modulus $B(V)=-V[dP(V)/dV]$ and the dimensionless pressure derivative of the bulk modulus $B'=dB/dP$.

Calculations within density functional theory (DFT) (Refs. 1 and 2) carry a footprint of the approximation used to represent the electronic exchange-correlation (XC) functional. The two most common forms currently used are the local-density approximation (LDA) and the generalized gradient approximation (GGA). The GGA comes in several different versions.[3] Common forms implemented in widely used DFT software packages are Perdew-Wang-1991 (PW91, Ref. 4) and Perdew Burke-Ernzerhof-1996 (PBE96 Ref. 5). The approximation for XC is actually the main ingredient in the DFT that shows a notable effect on the calculated EOS. The influence of other "technical" choices (such as choice of the basis, of the pseudopotential, or of an all-electron treatment) turn out to have only marginal effect (see, e.g., the detailed comparisons reported in Ref. 6).

It has been well known that the DFT calculations on solids (we consider simple nonmagnetic systems) usually underestimate the equilibrium lattice constant when the LDA approximation for XC is used, and overestimate it when the GGA is employed. Thus it does not surprise when the entire experimental $P(V)$ EOS turns out to be *bracketed* by the LDA and GGA results, as demonstrated by the examples shown in Fig. 1. For making comparison, several recipes, purely phenomenological or theory motivated, are described in the literature to correct for offsets between calculated and experimental values of V_0 and B_0.[9–13] For instance, a constant shift in pressure was applied to calculated $P(V)$ relations in Refs. 9, 11, and 13. Plotting the pressure against the relative volume V/V_0 is another frequently used choice.

In spite of a considerable volume of DFT calculations on $P(V)$ accumulated during the last decade, it has remained largely unnoticed that LDA and GGA results for the $P(V)$ of a given solid, such as shown in Fig. 1, are actually less different than they may seem.

In this paper, we show that there exists a simple scaling of V and P variables which, in regular solids, brings $P(V)$ variations like those shown in Fig. 1 to nearly a coincidence—making thus from the choice of the "better performing" XC form, see, e.g., Refs. 14–16, a secondary issue as far as the $P(V)$ is concerned, and offering a robust extrapolation-prediction scheme rather than merely two limits for the uncertainty. The idea was first mentioned in Ref. 17 and here we will document the validity of this empirical relation existing between different data on $P(V)$ on selected examples. We argue that regarding *nonlinear* elasticity, the DFT has predictive power at the quantitative level. One of the consequences is that DFT calculations of simple systems, i.e., systems with stable electronic (magnetic) ground state, can be considered sufficiently accurate to establish a pressure scale for experimental studies in the megabar range.

II. CALCULATIONS

For this work, results for total energies of c-BN, Na, Al, Pt, Au, BaF_2, and BaO_2 were obtained by LDA- and GGA-PW91 (Ref. 4) calculations. For most of these systems, a multitude of DFT-based EOS calculations is reported in the literature. However, for our purpose, we prefer to use the "raw" data for $E(V)$ and $P(V)$ which usually are not available in tabulated form. Hence, we have performed our own calculations in plane-wave basis, using projector-augmented

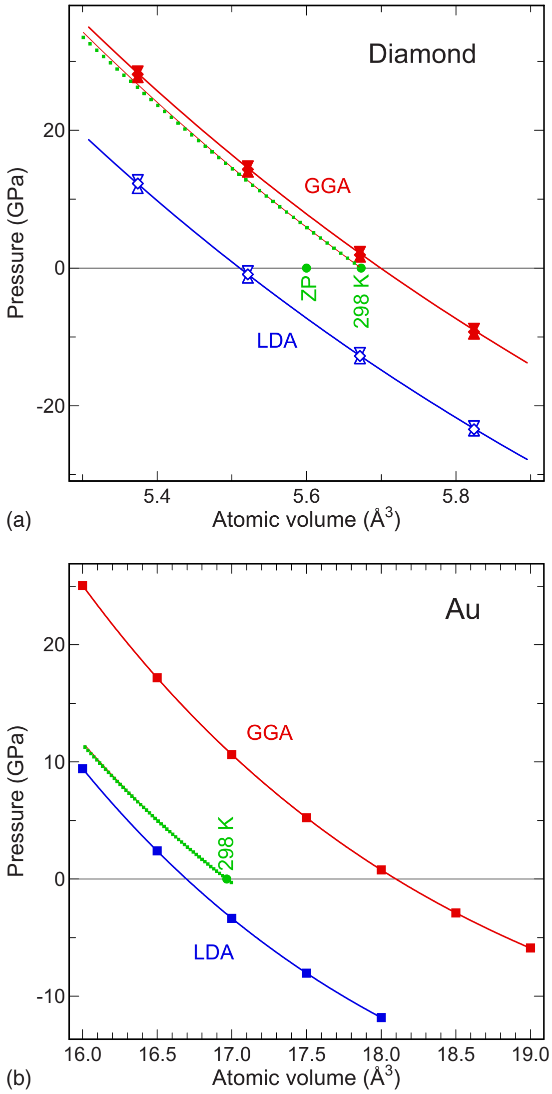

FIG. 1. (Color online) Pressure-volume relations from DFT calculations showing typical approximation-dependent differences in the predicted $P(V)$ behavior. (a) Diamond from Ref. 6; calculations by three different methods using LDA and GGA in each case. (b) Au (fcc), calculated near the experimental equilibrium (this work). Experimental data (300 K) are taken from Refs. 7 and 8. Zero-point (ZP) corrections are relatively large for diamond. Hence, the estimated experimental zero-point volume of diamond is indicated.

wave potentials[18,19] as implemented in the VASP codes.[20,21] We summarize the technical details as follows. The plane-wave cutoffs used were: c-BN 500 eV; Na (7 valence +semicore electrons) 375.0 eV; Al 301.2 eV (LDA) and 300.5 eV (GGA); Pt (10 valence+semicore electrons) 287.8 eV; and Au (11 electrons): 287.3 eV. In the barium compounds (Ba with 10 valence+semicore electrons, and potentials denoted in the VASP database as F_h and O_h), the cutoffs were 965.4 eV (LDA), 875 eV (GGA) in BaF_2, and 956.8 eV (LDA), 875 eV (GGA) in BaO_2. The Brillouin-zone integrations were performed on Monkhorst-Pack meshes[22] $20\times 20\times 20$ (770 irreducible **k** points) in fcc metals, $30\times 30\times 30$ (744 **k** points) in bcc metals, $6\times 6\times 6$ (28 **k** points) in BN, $8\times 8\times 8$ (60 **k** points) in BaF_2, and $4\times 4\times 4$ (11 **k** points) in BaO_2; the broadening of 0.2 eV was used in the treatment of all metallic systems (method of Methfessel-Paxton[23] to the first order).

The calculated "data" are analyzed by fitting a suitable third-order empirical equation of state (EEOS) expression such as Rydberg-Vinet,[24] Davis-Gordon,[25] modified Rydberg,[6] Holzapfel AP1,[26] Bardeen,[12,27] or Birch[28] to pressures (energies in the case of Na) as a function of volume. Here, suitable means that the EEOS form is chosen carefully so as to provide the best optimization by the usual statistical criteria. So, besides equilibrium volume V_0 and bulk modulus B_0, the optimization gives two pieces of information, namely, the value of the pressure derivative of the bulk modulus B_0' at the calculated V_0 and the type of third-order EEOS relationship that best reproduces a full set of calculated data. The value of B_0' characterizes nonlinear elasticity in lowest order. Identifying the optimal EEOS form is equivalent to finding, on a discrete "mesh," the best description of the higher-order nonlinear elasticity for a given substance. Actually, the sequence of EEOS relationships as given above is arranged in order of increasing "lattice potential anharmonicity" (see below). All results, consisting of V_0, B_0, and B_0' as well as the information on the optimal EEOS form, are collected in Table I. The table also lists results for diamond,[6] Ta,[40] α-Al_2O_3,[41] Li_2O,[42] and $LiCoO_2$.[38]

III. SIMPLE SCALING OF DFT RESULTS

We introduce dimensionless quantities V/V_0 (reduced volume) and P/B_0 (reduced pressure). It is understood that V_0 and B_0 are the DFT predictions when used with the calculated $P(V)$. In simple terms, we are proposing the combined substitution,[43]

$$V^{(\alpha)} \rightarrow \frac{V^{(\alpha)}}{V_0^{(\alpha)}}, \quad P^{(\alpha)}(V) \rightarrow \frac{P^{(\alpha)}(V)}{B_0^{(\alpha)}}. \tag{1}$$

where (α) stands for LDA or GGA (or experiment, see Sec. IV).

Replotting the data of Fig. 1 in reduced coordinates (Fig. 2) we observe that *both* sets of calculations offer an excellent agreement between each other. The differences between the calculated $P(V)$ relations nearly disappear, at least for pressures up to $P/B_0 \approx 1$. More precisely, at $P/B_0 = 1$, the scatter in P/B_0 is 1%. So, independent of the computational method and other approximations used, all calculations for diamond and Au give nearly identical results for $P(V)$'s in reduced coordinates.

We can look at more examples, cf. Fig. 2(c), of the effect of the scaling. Using the tabulated DFT results for the insulator α-Al_2O_3 reported in Refs. 41 and 44, it can be shown that at a volume change of 35% ($\sim P/B_0 = 1$), the LDA-GGA difference in P/B_0 is $\lesssim 2\%$. For Ta (a bcc metal), when comparing the various calculated LDA and GGA results of Boettger,[40] one finds a maximum difference in P/B_0 of only 2% at 40% compression ($\sim P/B_0 = 1.4$). These and other examples tested so far, cf. Table I, lead to the same conclusion: in the reduced coordinates, the LDA and GGA results nearly coincide and provide essentially the same *dimensionless*

TABLE I. DFT-calculated EOS results for selected elemental solids and compounds. Listed is the empirical EOS expression which best reproduces the calculated static lattice properties in the given range of volumes. For LDA and GGA, the obtained results are listed as triples of volume V_0 in cubic angstrom per atom, bulk modulus B_0 in gigapascal, and pressure derivative of the bulk modulus B_0'. The last column list experimental data for B_0' at 300 K, some entries referring to compilations. The upper part of the table is from this work and the lower part is taken from the literature.

Phase	V/V_0	EOS form	LDA (V_0, B_0, B_0')	GGA (V_0, B_0, B_0')	EXP 300 K B_0' and Ref.
c-BN	0.7	Holzapfel AP1	5.747,405,3.55	5.955,376,3.58	3.50–3.62 (Ref. 29)
Na bcc	0.48	Birch	33.283,9.0,3.87	37.198,7.4,3.83	3.88 (Ref. 30)
Al fcc	0.5	Rydberg-Vinet	15.800,84,4.61	16.544,76,4.63	4.14–4.83, see Ref. 31
Pt fcc	0.6	Mod. Rydberg	14.860,308,5.41	15.785,247,5.54	5.3–5.8, see Ref. 32
Au fcc	0.66	Mod. Rydberg	16.696,195,5.82	18.100,140.9,6.01	5.9 (5.0–6.5), see Ref. 33
BaF_2 fluorite	0.74	Holzapfel AP1	18.848,71,4.95	20.302,57,4.89	4.90 (Ref. 34)
BaO_2 bct	0.81	Rydberg-Vinet	15.861,89,5.05	17.143,70,5.13	n. a.
Diamond[b]	0.6	Mod. Rydberg	5.510,465,3.63	5.697,433,3.67	4.0(5), 3.0(1) (Refs. 7 and 35)
Ta bcc[a,c]		Bardeen	17.36,207,3.81	183.8,184,3.79	3.83(5) (Ref. 36)
α-Al_2O_3 [d]	0.65	Rydberg-Vinet	8.10,248,4.13	8.736,223.8,4.20	4.30(0.15), see Ref. 17
Li_2O a-CaF_2 [e]	0.67	Birch	7.604,94,3.95	8.345,80,3.98	5.2 (nonhydr.) (Ref. 37)
$LiCoO_2$ trig.[f]	0.72	Birch	7.618,169,4.67	8.237.143,4.51	4.1(3) (Ref. 38)

[a] Reference 39 reports similar results.
[b] Reference 6.
[c] Reference 40.
[d] Reference 41.
[e] Reference 37.
[f] Reference 38.

EOS to within less than 2% of scatter at $P/B_0 \approx 1$, as a rule. In terms of absolute pressure, this is smaller than the recently proposed corrections to the ruby pressure scale at around 100 GPa.[17]

One consequence of the scaling Eq. (1) is emergence of an approximate relation between the LDA and GGA equations of state given by

$$P^{\mathrm{GGA}}(V/V_0^{\mathrm{GGA}}) = P^{\mathrm{LDA}}(V/V_0^{\mathrm{LDA}})\frac{B_0^{\mathrm{GGA}}}{B_0^{\mathrm{LDA}}}. \qquad (2)$$

We observe that, even if the two approximations for exchange-correlation may differ on the "elementary level" (electrons), their distinct effects on an integral quantity such as P can be brought to merely scaling two variations. This observation is nontrivial because, clearly, on the "microscopic level," the use of LDA or GGA can lead to substantial *qualitative* differences in atomic properties. Working in reduced coordinates thus leads to the conjecture that, independent of the approximation for the exchange-correlation potential, DFT calculations for a given material provide consistent and nearly identical results on the dimensionless EOS, i.e., when P, V are transformed as in Eq. (1).

Referring to Figs. 1 and 2, the reduced coordinates Eq. (1) allow us to visualize the differences in $P''(V)$ between two EOSs so that we are left with comparing different variations in $B'(V)$. This dimensionless part of the calculated EOS is the key piece of information about a large-compression EOS from DFT theory. The $B'(V)$ is given by

$$B'[P(V)] = \frac{dB}{dP} = -\frac{V}{B}\frac{dB}{dV} = -1 - V\frac{E'''}{E''}. \qquad (3)$$

From the last equality, we see that B' is the dimensionless negative ratio of third to second volume derivative of E, offset by -1. As the leading term of the expansion for ΔE in isotropic volume compression is $\Delta E = B(\Delta V)^2/(2V)$—analogous to the harmonic term of the expansion $\Delta E = (\omega^2/2)\Sigma M_i u_i^2$ in the case of atomic vibrations—the "nonconstancy" of B (i.e., the volume dependence of B) reflects the "anharmonicity" of the $E(V)$ curve. The derivative $B'(V)$ is thus analogous to the Grüneisen parameter $\gamma(V)$ which appears in the context of phonons. Note that for a "harmonic" solid (characterized by a force between identical nearest-neighbor atoms that is linear in the relative atom displacement), it holds $B_0' = 1$, with only weak dependence of B' on volume. The vibrational analogy is $\gamma(V) = 1$ describing quasiharmonic oscillators.

Figure 3 shows examples of calculated $B'(V/V_0^{\mathrm{calc}})$ for diamond, gold, and Al_2O_2. As mentioned, the relationship $B'(V/V_0^{\mathrm{calc}})$ is extracted from calculated EOS data by fitting a suitable EEOS expression. The LDA and GGA results on $B'(V)$ shown in Fig. 3 do differ slightly when plotted versus reduced volume. It is instructive to retrace where do the small differences come from. Figure 4 offers a related illustration for the case of gold. At any given volume, the GGA reduces $B'(V)$ relative to LDA but the reduction becomes overcompensated when going to the larger GGA equilibrium volume at which B_0' (GGA) is to be taken so B_0' of GGA ends

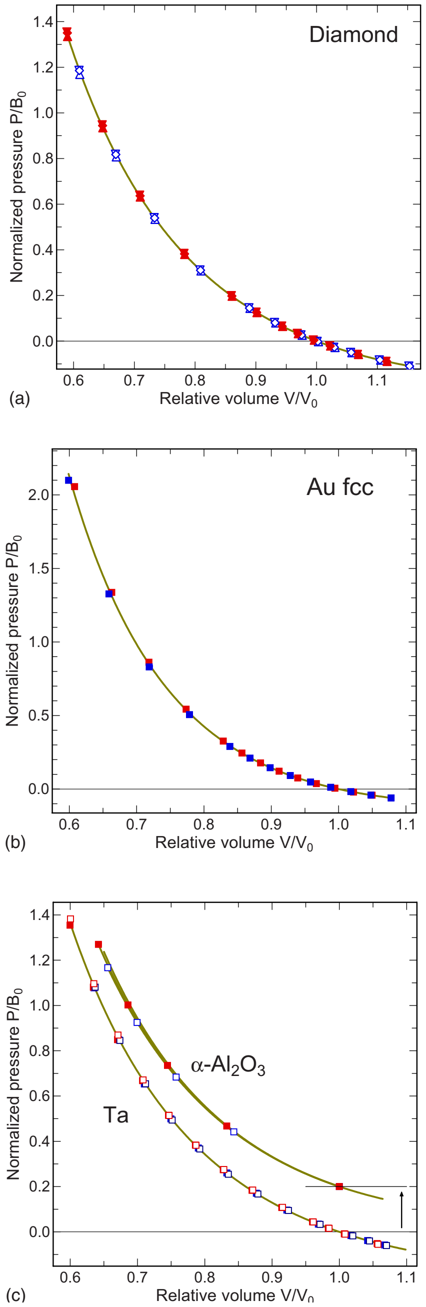

FIG. 2. (Color online) The data of Fig. 1 replotted in reduced coordinates after Eq. (1) and for an expanded range, panels (a) and (b). Also shown (c) are reduced-coordinate plots for bcc tantalum of Boettger (Ref. 40) (scalar relativistic and full relativistic LDA and GGA results) and (with vertical offset) for α-Al$_2$O$_3$ (corundum) using the calculated data of Refs. 41 and 44.

by being somewhat larger compared to B_0' of LDA. Gold, the example in Fig. 4, is one of the less favorable cases in the present context; the LDA-GGA difference in B_0' amounts to about 0.25 but this is still less than 5% of B_0'. In many cases, the GGA-LDA difference in B_0' is ~0.1 (3% relative) or less, such as for diamond. Hence, these and other examples lead us to the conclusion that different choices of approximation for the XC functional have little effect (to the first order) on the pressure derivative of the bulk modulus $B'(V)$. More specifically, the differences can be classified as small when compared to the experimental uncertainties or scatter in the values of B_0' (arrows at $V/V_0=1$ in Fig. 3).

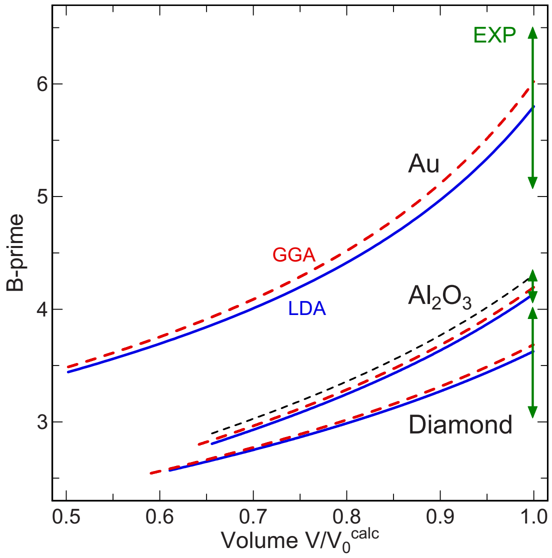

FIG. 3. (Color online) Calculated dependence of B' on reduced volume for selected substances. Curves are extracted from calculations of Ref. 6 (diamond), Ref. 44 (black dashed curve), and Ref. 41 (Al$_2$O$_3$), and this work (Au). Where available, both LDA and GGA results are shown. Vertical double arrows indicate the total spread of reported experimental data for B_0'.

The near agreement between scaled $P(V)$ relations for

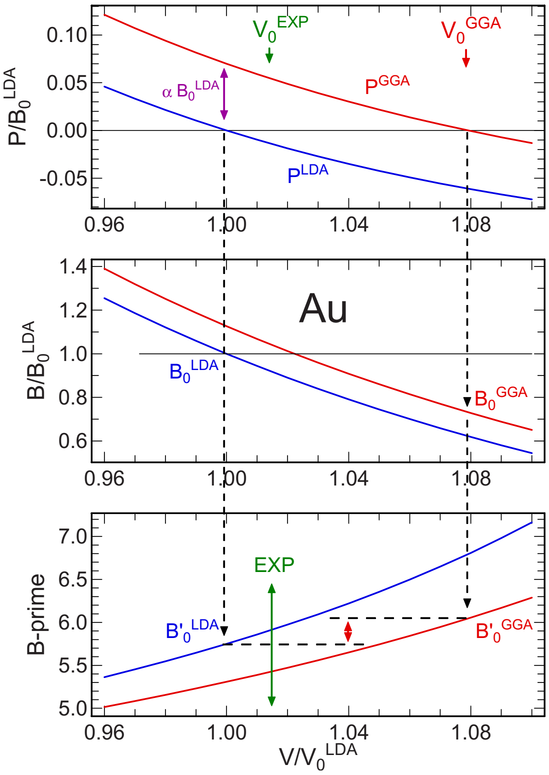

FIG. 4. (Color online) A zoomed view at the LDA-GGA differences of the calculated EOS of gold shown in Fig. 1(b). The ensuing $B(V)$ and $B'(V)$ are given as well.

LDA and GGA examples considered so far implies that (i) *the values of* B_0' *in* LDA *and* GGA *are nearly identical* and (ii) *the optimal* EEOS *form for a given substance is independent of* XC. Inspection of Table I shows that this not only applies to the examples picked for the above demonstration but also to all candidates listed in the table.

IV. SCALED DFT AND EXPERIMENT

Besides assisting us in judgments on the agreement between two calculated $P(V)$ variations, the scaling Eq. (1) is also, and above all, a *prescription* for *correcting* the theoretical predictions of $P(V)$ for the small discrepancies in V_0, B_0 with respect to experimental data. Actually, the rule Eq. (1) was initially meant to facilitate comparisons between theory and experiment. For this purpose, both the calculated volume and pressure are rescaled so as to match the experimental properties at zero pressure. These manipulations are fairly obvious and imply that we are adopting the experimental values of V_0 and B_0 and combine them with the dimensionless part of the calculated EOS. It should perhaps be emphasized that we are not considering situations where V_0, B_0 show a gross disagreement between experiment and theory.

Experimental data for B_0', mostly from acoustic measurements, are listed in the last column of Table I. For a given substance (phase), besides quantitative agreement, the scatter of the calculated B_0' values is always smaller than the experimental uncertainty. In other words, different approximations within DFT lead to a consistent result for $B'(V/V_0^{\text{calc}})$ *and* calculated values of B_0' appear to be *at least* as reliable as experimental information on nonlinear elasticity available at this point. The situation is reminiscent, in another context, of the pressure derivatives of band gaps: the latter are also predicted correctly by DFT calculations[45] whereas the absolute values of the quantities calculated at any given pressure, i.e., the gaps, can be largely off.

At this point, the available experimental data for $B'(V)$ cannot serve as a stringent test of the $E(V)$ anharmonicity evidenced by DFT because their systematic uncertainties are usually too large. Turning the argument around means that the DFT-calculated $B'(V)$ of standard systems, e.g., diamond, Al_2O_3, Al, Au, Ta, or Pt, appears sufficiently accurate for the purpose of generating a practical pressure scale for the 150 GPa range.

V. A CLOSER LOOK AT CALCULATED PRESSURES

The simple scaling of LDA-GGA results according to Eq. (1) is fully acceptable if the differences in $P(V)$ that remain after scaling are compared to the scatter and possible systematic errors in scaled experimental data. Although "universal" (no adjustable parameters needed), the scaling is approximate.

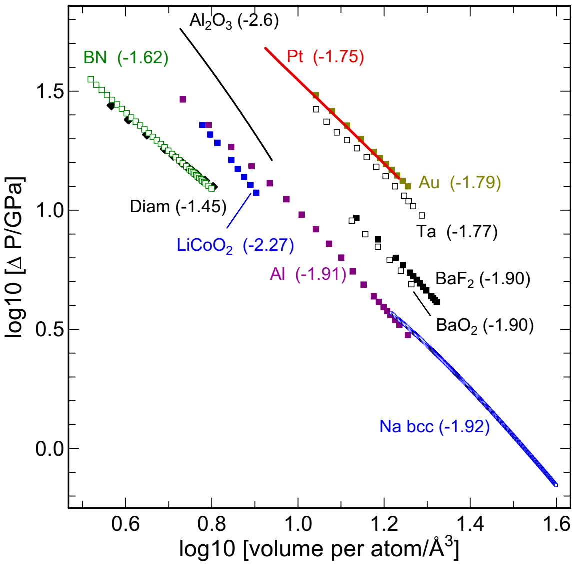

FIG. 5. (Color online) Double-log plot of the difference in calculated pressure $\Delta P = P^{\text{GGA}} - P^{\text{LDA}}$ as a function of volume per atom. Data from this work and Refs. 6 and 40–42. Numbers in parentheses refer to the exponent ξ in Eq. (4a).

Figure 5 shows the pressure differences $P^{\text{GGA}}(V) - P^{\text{LDA}}(V)$ versus (average) volume V per atom (ion). Despite the fact that in the logarithmic representation, the pressure and volume ranges are much compressed, it is clear that the data fall on nearly straight lines. Hence, they can be approximated by an inverse power law in volume (rather than an exponential dependence). So, we write pressure and bulk modulus as

$$P^{\text{GGA}}(V) = P^{\text{LDA}}(V) + \alpha B_0^{\text{LDA}} \left(\frac{V}{V_0^{\text{LDA}}} \right)^{-\xi}, \tag{4a}$$

$$B^{\text{GGA}}(V) = B^{\text{LDA}}(V) + \alpha \xi B_0^{\text{LDA}} \left(\frac{V}{V_0^{\text{LDA}}} \right)^{-\xi}. \tag{4b}$$

For the range of examples included in Fig. 5, both the values of the scaling α and the exponent ξ show a significant variation. In particular, one finds $\xi > 4/3$ (stronger than simple Coulomb scaling) which seems to result from the DFT-inherent coupling between the XC functional and other terms in the total energy. We note the indication of a systematic trend: $\xi \approx 3/2$ for strongly covalent semiconductors (diamond, c-BN), $5/3 < \xi < 2$ for metals (Na, Al, Ta, Pt, Au), and simple ionic compounds (BaF_2, BaO_2), and $\xi > 2$ for layered insulating oxides ($Al_2O_3, LiCoO_2$).

It is not straightforward to relate the refined parametrization of the GGA-LDA difference that we look at here to the parametrized gradient corrections to exchange and correlation that enter into the XC energy functional of the electron-density distribution.[5,46,47] Apparently, it is an averaged density gradient and averaged electron density that are reflected in the parameters α and ξ.

A practical consequence of the refined scaling: given an EOS calculated in LDA, Eqs. (4a) and (4b) can be solved for α and ξ if the values of V_0^{GGA} and B_0^{GGA} are known [$P^{\text{GGA}}(V_0^{\text{LDA}})$ and $B^{\text{GGA}}(V_0^{\text{LDA}})$ would also do]. Assuming that the power-law form of the GGA-LDA pressure difference applies more generally, an approximate $P^{\text{GGA}}(V)$ can be generated from $P^{\text{LDA}}(V)$ combined with a calculation in GGA near its equilibrium to obtain V_0^{GGA} and B_0^{GGA}. A similar procedure could, in principle, be applied when comparing $P(V)$

from LDA and experimental data. Given known values of V_0^{EXP} and B_0^{EXP}, an LDA calculation could be adjusted according to the above prescription and then serve as a prediction of the experimental $P(V)$. However, we would be entering into the scaling of higher-order effects which is not really justified in view of the fact that the simpler prescription Eq. (1) is fully adequate if errors of present-day experimental data are taken into account.

To work out the GGA-LDA difference for B', given a power-law dependence of the pressure difference, it is convenient to switch to dimensionless quantities. We take LDA as a reference and correspondingly the dimensionless volume, pressure, and bulk modulus are $v=V/V_0^{\mathrm{LDA}}$, $P(V)=P(V)/B_0^{\mathrm{LDA}}$, and $b(v)=B(V)/B_0^{\mathrm{LDA}}$. So, we write

$$p^{\mathrm{GGA}}(v)=p^{\mathrm{LDA}}(v)+\alpha v^{-\xi}, \tag{5a}$$

$$b^{\mathrm{GGA}}(v)=b^{\mathrm{LDA}}(v)+\alpha\xi v^{-\xi}. \tag{5b}$$

From the definition $B'=-(1/b)[v(db/dv)]$ and with

$$M(v)=\alpha\xi v^{-\xi}/b^{\mathrm{LDA}}(v), \tag{6}$$

we obtain

$$B'^{\mathrm{GGA}}(v)=B'^{\mathrm{LDA}}(v)\frac{1+M(v)\xi/B'^{\mathrm{LDA}}(v)}{1+M(v)}. \tag{7}$$

For realistic volumes $\xi/B'^{\mathrm{LDA}}(v)<1$, hence $B'^{\mathrm{GGA}}(v)<B'^{\mathrm{LDA}}(v)$. At $v=1$ (corresponding to V_0^{LDA}),

$$B'^{\mathrm{GGA}}(1)=\frac{B_0'^{\mathrm{LDA}}+\alpha\xi^2}{1+\alpha\xi}. \tag{8}$$

A consequence of the refined GGA-LDA scaling in Eqs. (4a) and (4b) is that the approximation for XC has essentially no effect on the optimum *analytical form* of the EEOS expression for a given substance. From Eq. (6), we can see why: the factor $M(v)$ fades away under compression because for realistic compression ranges $b^{\mathrm{LDA}}(v)$ always increases faster compared to $v^{-\xi}$. In other words, the functional form of $B'(V)$ for a given substance can safely be assumed to be independent of the choice for XC approximation.

VI. CONCLUSIONS

A simple scaling Eq. (1) applies to $P(V)$ relations calculated in LDA and GGA for a “regular” solid. The scaling Eq. (1) offers a recipe for translating the seemingly “ambiguously” calculated DFT values for $P(V)$ into each other. As the DFT calculations provide the material- and structure-specific variation $B'(V/V_0)$, nearly independent of the particular XC approximation and the computational method employed, it could be sufficient for comparison to experimental EOS data to calculate in just one approximation for XC and to normalize to experimental equilibrium volume V_0 and bulk modulus B_0, provided the experimental variation $P(V)$ is *bracketed* by the calculations in LDA and GGA.

The more general conclusion is that the XC approximations hardly differ when it comes to the prediction of *nonlinear* elasticity under hydrostatic pressure. Further, when compared to experiment, the predictions are well within the range of experimental values reported for B_0'. This leads to the view, pointed out by Martin:[3] DFT theory has potential in quantitative predictions of *nonlinear* elasticity which is a somewhat difficult terrain for experimental tests. This important aspect of DFT-calculated elasticity is hidden when a comparison of LDA and GGA results is made for calculated pressure, cf. Fig. 1, or bulk modulus at a given volume or for the bulk modulus at calculated zero pressure. To put it bluntly: the data from DFT calculations on *nonlinear elasticity* can be treated on a par with experimental results.

A question raised by this work is whether the very weak dependence of the derivative $B'(V/V_0)$ on the choice for the XC approximation, which was demonstrated here on selected examples, could be justified on a fundamental level, i.e., within the DFT itself.

Finally, our main message consists of (1) demonstrating the “equivalence” of the LDA and GGA predictions for the reduced $P(V)$ relationships, for a variety of *regular* solids; (2) identifying $B'(V)$, i.e., the nonlinear elasticity, as the essential EOS-related information provided by DFT calculations; (3) tacitly arguing in favor of calculations for obtaining data on $B'(V)$ in the low-temperature limit; (4) more generally, pointing out consequences for the nonlinear elasticity (XC approximations hardly differ and DFT calculations should be treated on a par with experimental results); (5) working out another simple relation between LDA and GGA, Eqs. (4a) and (4b), which perhaps will receive attention in future DFT studies; and (6) emphasizing that the optimal model-EOS form varies for different systems but for a given substance is essentially independent of XC.

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