Abstract: The rapid development of better high pressure experimental techniques combined with efficient and accurate density functional calculations of the structural properties of materials provide a new avenue to promote the study of materials at high pressures, which is currently based mostly on simple phenomenological modelling. The progress of experimental results into higher-pressure regimes represents a challenge to the phenomenological approaches, which can be addressed by carefully considered ab initio calculations. We present cold curves of several elements, calculated using different approximations of DFT and compare them with available experimental data. The comparison shows good agreement both in simple single phase and complex multi-phase cases. It suggests that DFT may be used to extrapolate high pressure behaviour of materials beyond the currently possible pressure range, with a robust estimate of the accuracy of the extrapolation based on various DFT implementations.

Keywords: Density functional calculations · Materials science · Elements · High-pressure

1. Introduction

The Kohn-Sham version of density-functional theory (DFT)\cite{1,2} is the most used quantum mechanical method for the calculation of the geometrical and electronic properties of solids. Calculations on a large variety of crystal structures are possible with relatively low cost and high accuracy.\cite{3} However, this computational efficiency requires choosing an approximate functional to represent the exchange-correlation energy, since the exact functional is unknown. The functionals of the local-density approximation (LDA)\cite{4,5} and the PBE implementation of the generalized gradient approximation (GGA)\cite{6} are the most common standard choices for calculations on periodic solids. While neither is uniformly accurate for calculations of all properties of all investigated solids, they do provide estimates for the atomic volumes of most solids with an accuracy of a few percent.\cite{7,8} The LDA overly favours homogeneity, and therefore underestimates the lattice constants and atomic volumes of solids. The PBE approximation, on the other hand, tends to overestimate those properties.\cite{7,9}

Consequently, it is possible to estimate the DFT error for the atomic volume of solids by comparing the results of these two approximations.

The behaviour of materials at high pressures has been attracting growing interest in the last two decades due to the rapid development of experimental techniques to measure their equations of state (EOS) under static and dynamic conditions. Measurements of the room temperature isotherms of materials at the Mbar regime are relatively recent. Therefore, the construction of EOS for metals, which are desired also at much higher pressures and temperatures, have traditionally depended on extrapolations from shock compression experiments. These extrapolations are based on semi-empirical models whose accuracy is difficult to assess and sometimes lead to inconsistencies with room temperature measurements.\cite{10} The expected accuracy of the cold curves extracted from these models is thus very rarely discussed.

In this paper we present the direct evaluation of cold curves of metals from ab-initio calculations as a feasible route to circumvent the inherent difficulties associated with extrapolations from shock compression data. We will concentrate on static measurements performed in diamond anvil cells (DAC) that currently often reach the 1 Mbar range.\cite{11,12} The modelling of these properties has been traditionally based on phenomenological approaches, such as the Birch-Murnaghan, and Vinet EOS.\cite{13,14,15} These EOS use simple thermodynamic considerations to extrapolate zero, or very low, pressure properties to high pressures. There is therefore no a priori justification to assume that they should remain accurate at high pressures, where the electronic and crystallographic structures of the materials could be significantly modified. Indeed, it is well known that pressure scales based on these phenomenological models show significant deviations that grow with increasing pressure and might reach the order of 10% in the Mbar range.\cite{16} These problems are obviously exacerbated for materials with multiple pressure-induced phase transforma-
tions, where extrapolations from low pressures are even less reliable.

The parallel advancements of experiment and theory have lead to a few attempts to improve EOS modelling using DFT calculations.\cite{15,16} Most of these have concentrated on the formulation of new pressure scales that would be consistent with DFT results for metals that preserve their crystallographic structure throughout the desired pressure range, e.g. Au, W and Pt.\cite{16} They still rely on the traditional phenomenological models and usually do not present clear estimates of the pressure-dependent error associated with the extrapolations to high pressures.

In this article we present calculations of the low temperature EOS, i.e. cold curves, of several elements, calculated using the LDA and PBE approximations of DFT and compare them with available experimental data. The results show good agreement for both simple single phase and complex multiphase materials, with LDA providing a lower estimate for the atomic volume at a given pressure and GGA providing a more accurate estimate with tendency to over-estimate the atomic volumes. These results suggest that DFT may be used to extrapolate high pressure behaviour of materials beyond the currently experimentally accessible pressure range, with a robust estimate of the margin of error of the extrapolation based on these two approximations of DFT.

2. The Cold Curves of Metals – Five Examples

The calculations presented in this section were carried out with three of the most commonly used DFT software packages. Two of them, VASP\cite{17} and Quantum Espresso (QE),\cite{18} are plane wave codes that use pseudopotentials to describe the interaction between ions and electrons. The third is the all-electron code WIEN2k,\cite{19} employing the Augmented Plane Waves plus local orbitals (APW + lo) formalism.\cite{20} The VASP software was employed within the AFLOW framework for computational materials science\cite{21,22} with projector augmented waves (PAW) pseudopotentials\cite{23} for both the PBE and LDA exchange correlation (XC) functionals. The QE runs used ultrasoft pseudopotentials (USPP)\cite{24} for both functionals. The total energies were calculated at fixed pressures (using the PSTRESS parameter in VASP and PRESS in QE) at zero temperature with spin polarization and without zero-point motion or lattice vibrations. All crystal structures were fully relaxed (cell volume and shape and the basis atom coordinates inside the cell). Adjusting the high-energy cutoff for the pseudopotentials and the density of the K-point Monkhorst-Pack meshes ensured numerical convergence to about 1 meV/atom. The VASP calculations were performed according to the AFLOW standard for material structure calculations,\cite{25} with a 6000 K-points or higher Monkhorst-Pack mesh and an energy cutoff 30% higher than that of the potential. The QE runs used a minimum cutoff energy of 100 Ry/atom and dense 48\^{}<sup>3</sup> Monkhorst-Pack meshes. The WIEN2k runs were performed at fixed volumes without relaxations on simple structures where the effect of structural relaxation is expected to be negligible. The radii of the muffin-tin spheres were 1.85 a.u. for Os and Ti, 1.75 a.u. for Al and Pb and 1.65 for Ga. A k-mesh of 10,000 points and a basis-set size of RmtKmax = 10 for Al and Pb, 9 for Os and Ti and 8 for Ga, were verified to provide an accuracy of $\sim 10^{-4}$ Ry in the total-energy calculations, with an energy cutoff separating core and valence states of $\sim 12$ Ry for Pb, $\sim 11$ Ry for Al, $\sim 8$ Ry for Ga and $\sim 7.5$ Ry for Os and Ti. The pressure was extracted from the slope of the calculated E(V) curve. These all-electron calculations were performed for comparison with the plane-wave codes to provide an assessment of the validity of the pseudopotential approximation over the investigated range of pressures.

2.1 Aluminium

The experimentally reported cold curve of aluminium includes two solid-solid phase transformations. At ambient conditions the stable phase is fcc. It is transformed to the hcp structure a little above 2 Mbar.\cite{26,27} As the pressure is further increased, coexistence of the hcp and bcc structures is observed over an extended range 3.0–3.8 Mbar. The bcc phase was shown to persist up to 4.75 Mbar.\cite{27}

DFT calculations reproduce this sequence of phase transitions but give transition pressures that are slightly lower than the reported pressure for the first transition, 1.8–2.0 Mbar, and slightly too high, 3.8–4.0 Mbar, for the second (Figure 1).

The measured volumes per atom at all phases agree well with the calculated volumes, mostly near the PBE results or inside the narrow range between the LDA and PBE (Figure 2). The VASP-PAW and QE-USPP calculations also agree well with each other and overlap in the figure. The noise in the measured volumes is of the same order of magnitude as the difference in the calculated volumes between the PBE and LDA approximations. As can be seen in Figure 2, the

![Figure 1. Enthalpies of the fcc (green) and hcp (blue) structures of aluminium, calculated in the PBE XC approximation, with PAW potentials of VASP (solid lines) and USPP of QE (dash-dot), compared with the corresponding calculations of the bcc structure (red x-axis).](image-url)
measurement noise increases with pressure, as the measurements become less accurate and the pressure scales become less reliable near the upper limit of the pressure achieved in the experiments. In contrast, the variance between the LDA and PBE calculations decreases with increasing pressure, from 4% at zero pressure to 2.3% at 1 Mbar and 1.5% at 5 Mbar, providing tighter predictions for the cold curve as the pressure is increased to the limit of current experiments and beyond.

As the pressure increases, and the atoms in the unit cell become more densely packed, the calculation of the atomic volume might be affected by the frozen core of electrons inherent in the pseudopotential approximations. To test the validity of these approximations we compare the volumes obtained for the densely packed fcc structure in the PAW, USPP and all-electron (black) calculations for the fcc phase in the PBE (solid lines) and LDA (dash-dot lines) approximations shows good agreement and thus the suitability of the pseudopotential approximations for this range of pressures.

2.2 Lead

At ambient conditions, the crystal structure of lead is fcc. As the pressure is increased, at room temperature, a phase transformation to the hcp structure has been identified experimentally at the pressure range of 110–190 Kbar. A second very shallow transformation to the bcc structure has been identified at pressures of 1.25–1.75 Mbar. Previous DFT calculations have shown the same order of structure changes at transition pressures of 130 Kbar and 0.9–1.1 Mbar, respectively. Thus the calculated pressure of the first transition agrees well with experiment but that of the second is too low. The volume changes obtained at both structure transformations are very small, less than 1%, in the experiments as well as in the calculations.

Our calculations reproduce the fcc-hcp transition near 190 Kbar with a small volume change of about 0.5%. The hcp-bcc transition is obtained near 2.2 Mbar, considerably above the measured range (Figure 3). At a higher pressure, 6.5–7 Mbar, beyond the current measurements, we obtained a reverse transition from bcc to hcp. The volume changes in the two higher transitions are negligible, ~0.1%.

The measured volumes per atom of the fcc and hcp phases agree well with the calculated volumes up to about 2 Mbar (Figure 4). In this range they lie between the LDA and PBE estimates. Around 2 Mbar the measurements become much noisier and deviate towards volumes up to 1% larger than indicated by the PBE calculations. This might again be explained by reduced accuracy of the measurements near the upper limit of their current range. The difference between the LDA and PBE calculations again decreases with increasing pressures, from 5% at zero pressure to 3% at 1 Mbar and 1.5% at 5 Mbar.

2.3 Gallium

The reported sequence of phases along the cold curve of gallium is quite complex and is not yet fully resolved. The stable phase at ambient conditions α-Ga is well established. It is an orthorhomic oS8 structure. At the relatively low pressure of 20 Kbar it transforms to a phase labelled GaII, which has previously been reported as a cubic c112 structure. However a more recent study suggested that this phase should be interpreted as having a much more complex orthorhombic oS104 structure. Early experiments reported...
the existence of three additional phases, \( \beta \)-Ga (monoclinic \( mS4 \)), \( \gamma \)-Ga (orthorombic \( oS40 \)) and \( \delta \)-Ga (rhombohedral \( hR66 \)), at very low pressures.\(^{35–37} \) These phases are now known to be metastable. The GaII phase is thought to persist up to about 300 Kbar, where it is transformed to the tetragonal \( tI2 \) structure, usually referred to as GaIII and identical to \( \alpha \)-In.\(^{38,39} \) However, an additional rhombohedral \( hR6 \) phase, labelled Ga-V, has been reported in the partially overlapping 100–140 Kbar range.\(^{34} \) At still higher pressures, the GaIII structure gradually transforms into the fcc structure around 1 Mbar. The fcc structure has been shown to persist up to 1.5 Mbar.\(^{40} \)

Our calculations reproduce quite well this complex series of phase transformations (Figure 5), including the very low-pressure phase transition from \( \alpha \)-Ga to GaII, the GaII to GaIII transition and the continuous relaxation of GaIII into fcc at pressures above 1 Mbar. Comparison between the two structures reported for GaII shows that the calculations support the recent report on the \( oS104 \) structure, which turns out with a slightly lower enthalpy than \( cI12 \). The proposed Ga-V structure is shown to be slightly metastable in the same pressure range indicated in the experimental report. Throughout this complex sequence of structural transformations, the measured atomic volumes are obtained between the calculated LDA and PBE atomic volumes of the respective structures (Figure 6), while the discrepancy between the two calculations decreases with increasing pressure from 6.5% at zero pressure to 3.5% at 1 Mbar and 1.9% at 5 Mbar.

2.4 Titanium

The cold curve of titanium includes five phases, a few of which only recently discovered, with pressure and temperature stability ranges that are not yet well characterized.\(^{41–45} \) The well-known stable phase at ambient conditions is hcp, usually
denoted as α-Ti. At low pressures, in the range of 20–120 Kbar a transformation occurs to the hexagonal ω phase (hp3).\(^{[45,46]}\) The ω phase is also known to be the stable structure at low temperatures, as titanium is cooled below ambient temperatures at ambient pressure.\(^{[42,47,48]}\) At higher pressures, various reports were published on the appearance of an orthorhombic phase near 1160 Kbar, denoted the γ-phase,\(^{[41]}\) or on a complex phase transition in the pressure range 1280–1400 Kbar, where γ is just an intermediate phase that quickly transforms to a different orthorhombic structure, denoted as the δ-phase.\(^{[42]}\) Both these phases are characterized by Pearson symbol oP4 and space group #63. The differences between them are subtle and make accurate identification quite difficult. Both structures are reported to be slight deformations of higher symmetry structures. The γ-phase is a slight distortion of the hcp structure, while the δ-phase is a slight distortion of the bcc structure.\(^{[46]}\) At still higher pressures an additional transition to the bcc structure has been predicted by ab initio calculations.\(^{[49,50]}\) This transformation has not yet been observed in experiments in diamond anvil cells, up to pressures of 2.2 Mbar.

Our DFT calculations of the zero temperature enthalpies of the different phases reflect this complex experimental picture (Figure 7). At low pressures, the hexagonal ω phase is the stable structure, with a little lower enthalpy than the hcp structure. As the pressure is increased to about 1 Mbar, the ω, γ and δ structures become nearly degenerate. They have nearly the same enthalpy in a narrow range around this pressure. As the pressure is further increased, the δ structure emerges as the most stable phase until it gradually relaxes to the bcc structure at 1.5 Mbar. At low pressures the γ phase is unstable and relaxes into the hcp structure, in agreement with the observation that γ is a slight distortion of hcp that emerges only at intermediate pressures. The relaxation at high pressure of the δ structure into the bcc phase also conforms to the observation that one is a slight distortion of the other.

The atomic volumes calculated for all phases in the PBE approximation also agree quite well with the experiments, as shown in Figure 8. In particular, the atomic volumes of the γ and δ phases agree well with the experiments near the complex phase transition at 1–1.5 Mbar. Near 2 Mbar, the calculated atomic volume of the δ phase becomes a little lower than the measured volume. This might be a result of larger measurement errors at the end of the measurement range or due to the approaching gradual transition to the bcc phase that is not clearly observed in the experiments but might influence the interpretation of the measured XRD diffractions. Again, the LDA calculations provide lower limits on the atomic volumes for all phases. The discrepancy between the LDA and PBE calculations decreases with increasing pressure from 6.3% at zero pressure (ω phase) to 5% at 1 Mbar (δ-phase) and 2.8% at 5 Mbar (bcc).

2.5 Osmium

Osmium has a very simple single structure cold curve. The hcp structure has been shown to persist from ambient pressure up to about 7.5 Mbar, the highest static pressure ever reported in DAC measurements.\(^{[51]}\) Nevertheless, osmium has attracted much experimental and theoretical attention because it is the densest and most incompressible metal. There was even a
claim,\textsuperscript{[52]} later detracted,\textsuperscript{[53]} that it is less compressible than diamond and that it exhibits structural anomalies attributed to topological transitions in the Fermi surface while preserving the hexagonal close-packed phase.\textsuperscript{[51]} The most recent report on its properties, up to a pressure of 2 Mbar at ambient temperature, does not provide any evidence for either claim, but shows a simple contraction with increasing pressure that is well within the theoretical description provided by DFT calculations.\textsuperscript{[54]}

Figure 9 shows our calculations of the atomic volume as a function of pressure compared to the two most recent sets of measurements. The first set, that reached the record setting DAC pressure of 7.5 Mbar\textsuperscript{[51]} starts, as with most other metals, between the LDA and GGA estimates, but then veers towards lower volumes at pressures as low as 0.5 Mbar and breaks considerably below the LDA results at pressures above 2 Mbar. The newer set, accompanied by much tighter estimates of the measurement errors, stays within those computational estimates up to 2 Mbar.\textsuperscript{[54]} These differences have been attributed to considerable inhomogeneity of the pressure in the record setting DAC setup, as well as to growing inaccuracies of the pressure scales at pressures above 1 Mbar.\textsuperscript{[54,55]} The second set demonstrates that more careful pressure measurements indeed preserve the experimental results within reasonable limits of the DFT estimates. The deviation above 2 Mbar might still be due to a yet undetected phase transformation that might be revealed by extending the high accuracy measurements to higher pressures. Above 2 Mbar, the PAW calculations start deviating towards higher volumes compared to the USPP and all-electron results. This might be an expression of the frozen core effect that becomes more pronounced with increasing pressure and renders this pseudopotential less reliable at high pressures.

As in the previous examples, the LDA-PBE comparison provides an estimate for the margin of error of a few percent for the atomic volume as a function of pressure, both inside the range of current measurements as well as at much higher pressures. The discrepancy between the LDA and PBE calculations decreases with increasing pressure from 6.5\% at zero pressure to 3\% at 1 Mbar and about 2\% at 5–10 Mbar.

The examples presented above include both simple single phase and complex multi-phase materials, with sufficient experimental data up to 2 Mbar that allows for a meaningful comparison of experiments and calculations. It is shown that the LDA provides a lower estimate for the atomic volume at a given pressure and GGA is closer or sometimes over-estimates the atomic volumes. The expected accuracy of the cold curve derived from these calculations is provided by the difference between the LDA and PBE calculations of the unit cell volume and is of the order of a few percent. It should be noted that this assessment remains valid at the vicinity of the transition pressures between different phases, despite the greater uncertainty in the identification of these pressures, which may be higher than 10\%. While DFT calculations usually correctly predict or reproduce the order in which the phases appear with increasing pressure in experiments, the comparison of calculated and experimentally observed phase transition pressures entails two types of difficulties, one experimental and one computational. On the experimental side, finding an accurate equilibrium transition pressure (the pressure at which both phases can coexist in equilibrium) is quite challenging. It is subject to hysteresis, details of the measurement method, sample type and non-hydrostatic stress conditions. Thus, most transitions observed are not definite pressure points but rather pressure ranges, some of them quite extensive, as pointed out in the descriptions of the above examples. On the computational side, identifying the stable phase at any given pressure requires comparison of the enthalpies of structures that differ by merely a few meV/atom over a range of pressures around the actual transition. Thus, even well converged calculations may present discrepancies in the exact identification of the transition pressure, due to otherwise insignificant computational details. As demonstrated by our results, these discrepancies do not significantly affect the evaluation of the cold curve volume as a function of pressure, which is much less sensitive to those details. The associated volume changes are usually small, and the absence of sharp transitions is thus in line with available experimental data. It should also be noted that no systematic comparison of the computational and experimental phase transition pressures yet exists in the literature, even for the elements. Such a systematic analysis would certainly be in order for future studies.
3. Summary

The conclusions of the comparison between DFT EOS and the experimental data for the five examples presented above can be summarized as follows. First, the DFT results are rarely outside the uncertainties of the experimental data, despite the fact that we have only used a rough comparison that ignores the small effect of the thermal expansion difference between the zero temperature calculations and the room temperature measurements. This discrepancy does not exceed a few percent at ambient pressure and becomes negligible at high pressures.

Second, up to about 2 Mbar, the DFT results provide excellent estimates of the experimental data, with LDA providing a lower estimate of the atomic volume and PBE very close to the measurements. Above this pressure, the experimental data may slightly deviate from those estimates, an effect that might be attributed to reduced accuracy of the measurements near the upper limit of their range. Indeed, a recent comprehensive study of the cold curves of the elements up to 1 Mbar concluded that the DFT error at higher pressures is always equal or smaller than at very low pressure.31 There is no reason to expect that this trend would change as the pressure is increased beyond 1 Mbar. On the contrary, as pressure is increased the electronic density distribution over the unit cell becomes more homogeneous, and should therefore be described more accurately by the DFT approximations. Thus, the difference between the LDA and PBE results for the atomic volume may provide a good estimate of the expected error on the DFT-calculated EOS at arbitrarily high pressures.

Third, the variance between the LDA and PBE estimates of the atomic volume decreases as the pressure is increased. Therefore, this approach provides improved tighter margins for the errors of the EOS with increasing pressure.

These three conclusions suggest that DFT calculations can be used as a good basis for an accurate extrapolation of the EOS of materials to high pressures, well beyond the pressure range currently available to experiments. This approach might be used as a good basis for an accurate extrapolation of the EOS to high pressures, and does not change the conclusions detailed above.

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References

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