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Density Functional Theory (DFT) calculation of the FCC cold curve for silver

Luke Shulenburger
Thomas R. Mattsson
HEDP Theory
Sandia National Laboratories
Albuquerque, NM 87195-1189

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Abstract

This memo summarizes the results of all-electron density functional theory (DFT) calculations of FCC Silver under pressure. Particular emphasis is placed on the effect of exchange correlation functional and the behavior at high pressures. We find that the AM05 and WC functionals produce results which agree better with experiments at ambient pressure than functionals like the LDA or GGA. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

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1 Introduction

A common approximation when developing an equation of state model for an element is to separate the free energy, F, into ionic and electronic components as follows

$$F = F_c + F_i + F_e, \tag{1}$$

where F_c, F_i, and F_e are respectively the cold curve, thermal ionic, and thermal electronic contributions. The cold curve is the energy as a function of density at zero temperature while thermal contributions from electrons and ions are positive, raising the energy and pressure from the cold curve level.

Since the cold curve acts as a floor for the free energy, it is very important to employ a cold curve of high fidelity. Density Functional Theory (DFT) has been applied for a long time to calculate cold curves, from the beginning using the Local Density Approximation (LDA) and for the last 15 years also using the Generalized Gradient Approximation (GGA), for example PBE[1]. The two approximations differ, however, in how well they describe different materials, and FCC silver is a particularly difficult material. LDA "overbinds" silver significantly with a too short lattice constant and a too high bulk modulus while PBE yields a too large lattice constant and a too low bulk modulus. Over the last few years, there has been progress made in density functionals, the Armiento-Mattsson (AM05)[2] and and Wu-Cohen[3] functionals significantly improve upon LDA and PBE. In this memo, we present results for the cold curve for FCC silver using four functionals.

2 Method and Parameters

In this memo, the equation of state of FCC Silver is calculated as a function of pressure at zero temperature. In order to remove the effect of pseudopotentials, all electron LAPW[4] density functional theory calculations are performed using elk[5]. Although no pseudopotentials are used in the LAPW method, there is a partitioning of electrons into core and valence for reasons of computational efficiency (eg. the core electron wavefunctions are only calculated inside the muffin tin surrounding each ion). In elk the scheme used is actually better classified as LAPW+lo with localized orbitals added to the basis set. In this case the 4s, 4p, 4d and 5s electrons were treated as valence states and six local orbitals are used. The muffin tin radius for the Ag was set to 1.8 Bohr and kept fixed for all calculated volumes. The convergence of the basis set is governed by the maximum length of the G vectors in reciprocal space. In this case good convergence was achieved for all volumes by specifying $r_{mt} * |G_{max}| < 11.5$.Also the maximum angular momentum for the APW functions was set to 12 and 10 for the potential and density. Finally, because FCC Ag is a metal over the range of pressures considered here, care was taken in converging the k-point grid. In these calculations, the 1 atom primitive cell was used and the energy was well converged using a 14x14x14 grid of k-points with Gaussian smearing using a width parameter of 0.001 Ha.

3 Results

The total energy was calculated at 33 different values of the lattice parameter ranging from 5.125 Bohr to 9.25 Bohr using four different exchange correlation functionals: LDA[6], PBE[1], AM05[2], and Wu-Cohen[3]. The Energy vs Volume curves are plotted in Fig 1

Qualitatively these results differ in their treatment of silver both at high pressure and near equilibrium. Near equilibrium these differences can be quantified by fitting the data to a standard equation of state and comparing the equilibrium volume, bulk modulus and

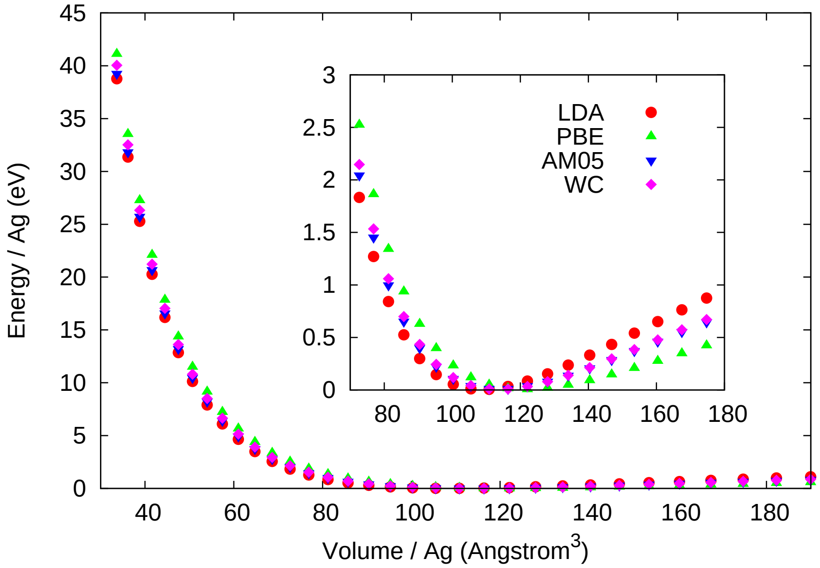

Figure 1: Energy versus Volume for FCC Ag using four different exchange functionals.

derivative of the bulk modulus. As shown in Table 1, the newer generation of GGA functionals, represented by AM05 and WC agree very well with the experimental values cited in Ref.[7]. This is in contrast with LDA which predicts Ag to be too hard and with a smaller lattice constant and PBE which predicts the material to be too soft and with a larger lattice constant. Earlier FP-LMTO calculations using RSPT[7] are also included as a check on the current work.

	V_0 (Bohr^3/atom)	K_0 (GPa)	K'
Expt	113.66	109	-
LDA (RSPT)	108.78	137	-
LDA (elk)	108.89	138.8	5.67
PBE	121.10	91.6	5.86
AM05	113.35	114.5	5.75
WC	113.81	119.0	5.65

Table 1: Equation of state parameters for FCC Ag using four different functionals. All data is from calculations with elk except for that labeled RSPT, which was published in Ref.[7]

In determining the pressures in the high density regime some care is warranted. The Vinet fit used near the equilibrium value is actually somewhat too soft at high compressions, as can be seen for the LDA case in Fig 2. The same form fit only to the high pressure points is accurate in that regime, but fails around the equilibrium. For reference a b-spline fit to the data is included. This provides an accurate interpolation to the bulk of the data, but fails at

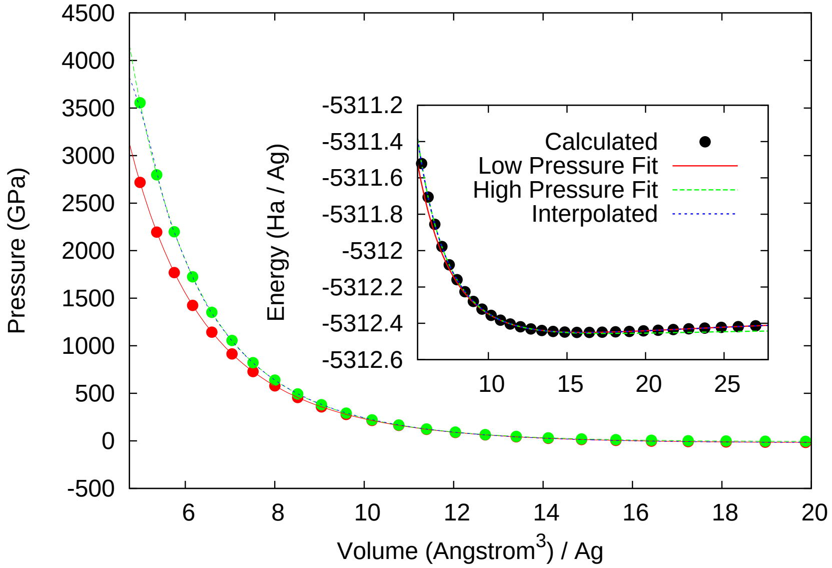

Figure 2: LDA data fit with Vinet equation ignoring both high and low pressure points. B-spline interpolation is included as a benchmark

the extremes of the calculated lattice constants due to poorly defined boundary conditions.

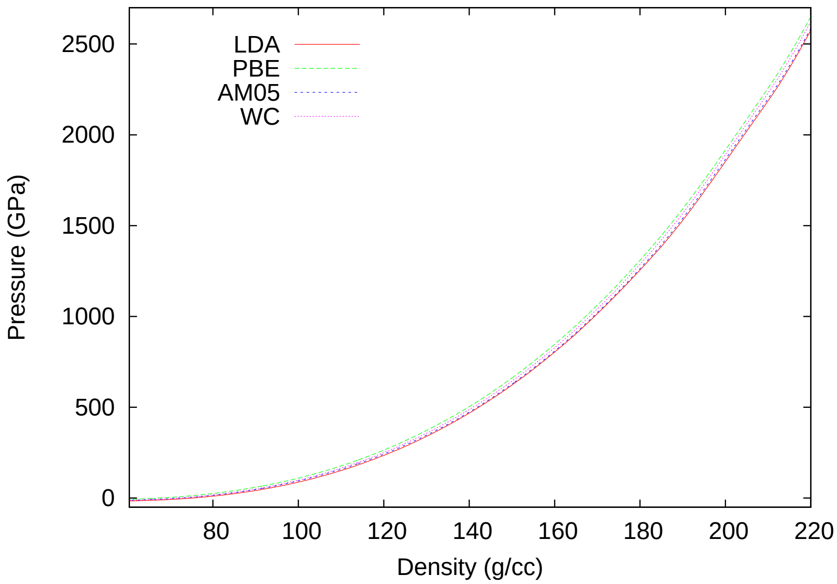

Figure 3: Pressure calculated using spline fit to data with 4 different functionals.

We conclude by including the calculated pressures using a spline interpolation of the data. These results are summarized in Fig 3.

4 Acknowledgment

Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

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A Energy as a function of volume for FCC silver

Volume (Bohr^3/atom)	LDA (Ha)	PBE (Ha)	AM05 (Ha)	WC (Ha)
33.6528	1.424716397	1.511069783	1.442343331	1.471449234
36.1757	1.152271337	1.232196003	1.169475651	1.194918814
38.8217	0.928874157	1.002146423	0.945128991	0.967351664
41.5937	0.744943777	0.812062133	0.759998341	0.779671144
44.4946	0.595015737	0.655990893	0.608964941	0.626059134
47.5273	0.472264327	0.527871483	0.485455301	0.500213394
50.6948	0.372015327	0.422650163	0.384544841	0.397173624
54.0000	0.290406767	0.336345253	0.302290561	0.312955354
57.4458	0.224240447	0.265760423	0.235466751	0.244363314
61.0351	0.170886937	0.208148903	0.181391701	0.188682014
64.7709	0.128122737	0.161231193	0.137763111	0.143673264
68.6562	0.094123027	0.123260923	0.102824401	0.107565194
72.6938	0.067393547	0.092758503	0.075115391	0.078880934
76.8867	0.046683227	0.068467353	0.053395381	0.056352814
81.2377	0.030940377	0.049320993	0.036630341	0.038915284
85.7500	0.019279877	0.034433363	0.023946221	0.025678574
90.4262	0.010962397	0.023066463	0.014687981	0.015915694
95.2695	0.005364787	0.014600223	0.008174861	0.008965154
100.2827	0.001979637	0.008516003	0.003895641	0.004329684
105.4687	0.000385697	0.004379433	0.001430831	0.001575004
110.8305	0.000230707	0.001814543	0.000405571	0.000332604
116.3710	0.001221347	0.000536293	0.000437211	0.000303244
122.0932	0.003109417	0.000192343	0.001371461	0.001231154
128.0000	0.005639177	0.000653743	0.002931181	0.002880774
134.0942	0.008710057	0.001751633	0.005063611	0.005127794
140.3789	0.012170257	0.003359043	0.007611361	0.007821924
146.8569	0.015921957	0.005375613	0.010499561	0.010868744
153.5312	0.019860597	0.007652323	0.013657811	0.014135574
160.4047	0.023903367	0.010139403	0.016937121	0.017541464
167.4804	0.028018897	0.012785663	0.020298971	0.021054354
174.7612	0.032149767	0.015533743	0.023689801	0.024633814
182.2500	0.036263327	0.018349233	0.027097481	0.028233564
189.9497	0.040335637	0.021196763	0.030408741	0.031828374

Table 2: Energy as a function of volume for FCC silver using four different exchange-correlation functionals, all energies are in Hartree.