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High-precision calculation of crystallographic phase-transition pressures for aluminum

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High-precision, all-electron, full-potential local density-functional calculations are used to reduce the uncertainty in static-lattice predictions of the high-pressure structural phase transitions in Al. These calculations predict a static-lattice fcc→hcp transition pressure of 205 ± 20 GPa and suggest a fairly firm upper bound of 290 GPa for the $T=0$ K fcc→hcp transition pressure. These results indicate that a recently reported diamond anvil cell experiment probably came very close to achieving the fcc→hcp phase transition in Al.

Determination of structural transition pressures in Al at $T=0$ K was the topic of three density-functional-theory (DFT), local-density-approximation (LDA) studies roughly a decade ago. Two of these, one by McMahan and Moriarty¹ and the other by Lam and Cohen² (MM and LC, respectively), used pseudopotentials rather than all-electron methods and obtained notably different predictions for the fcc→hcp transition pressure (MM 360 GPa vs LC 220 GPa), and the hcp→bcc transition (MM 560 GPa vs LC 380 GPa) (Ref. 3). MM also treated these transitions via the all-electron LMTO method in its spherically averaged rather than full-potential form. The linear muffin-tin-orbital (LMTO) predictions also differed substantially from the others: fcc→hcp at 120 GPa, hcp→bcc at 200 GPa. The fcc→bcc value was not reported by MM; LC found 300 GPa at $V/V_0 \approx 0.45$. Given that the extreme values for the transition pressures were obtained by MM using the same LDA, the wide variation in the results must be attributed to the different approximations (pseudopotentials and muffin-tin potentials) utilized.

A bit later a full-potential, all-electron, linear combination of Gaussian-type orbitals (LCGTO) calculation⁴ using the Kohn-Sham-Gaspar⁵ (KSG; i.e., X_α with $\alpha = \frac{2}{3}$) LDA found the fcc→bcc $V/V_0 = 0.446$, in good agreement with LC, but at a slightly higher transition pressure, 330 GPa. On the basis of that single comparison with all-electron, full-potential results, LC's *ab initio* pseudopotential predictions at least proved consistent, provided that the differences in LDA models were kept in mind. The LCGTO code used in Ref. 4 was restricted to cubic symmetries, however, so no direct resolution among the different predictions (MM, LC) was possible. In this admittedly restricted context, the best previously available prediction of $P_{\text{fcc} \rightarrow \text{hcp}}$ would seem to be LC's. Though there are several more modern calculations of the equilibrium lattice parameter, bulk modulus, and cohe-

sive energy of Al, *a priori* prediction of the transition pressures does not seem to have been pursued after Ref. 4.

A recent remeasurement of the equation of state (EOS) of Al by diamond anvil cell (DAC) techniques⁶ found no evidence for an fcc to hcp structural phase transition for pressures through 219 GPa ($V/V_0 = 0.50$), hence $P_{\text{fcc} \rightarrow \text{hcp}} \geq 220$ GPa (assuming no metastability at phase transition). This measurement reopens the issue of the disparity among the prior calculations, as follows.

The LDA, whatever its other well-known limitations, has yielded very reliable $T=0$ K equations of state. If the LDA were to turn out to fail in the case of a simple metal such as Al that failure would be a new constraint on the limits of the simplest approximations in density functional theory. Conversely, experimenters cannot exploit the supposed reliability of LDA equations of state when the existing predictions range over roughly 50–150 % of the most modern measurement of a bound on $P_{\text{fcc} \rightarrow \text{hcp}}$. If the lowest prediction, $P_{\text{fcc} \rightarrow \text{hcp}} = 120$ GPa (MM) were to embody the LDA accurately, then there is a serious conflict between experiment and theory. If, however, the intermediate prediction (220 GPa, LC) is correct (with some reasonable error bars), the DAC experiment came extremely close to achieving the fcc→hcp transition, and should be pursued vigorously. If the highest predicted pressure (360 GPa, MM) is the “best” LDA value, one of two dilemmas results. Either the predicted transition lies at experimentally forbiddingly high pressure (at least for the near future) or, if the actual $P_{\text{fcc} \rightarrow \text{hcp}}$ is only slightly above the Ref. 6 bound, once again a serious deficiency in the LDA has been exposed. If possible, the issue should be resolved on the calculations side prior to experimental determination of the transition pressure; otherwise the calculation simply becomes a confirmation and parametrization of the experiment. Clearly there is a need for high-precision, all-electron, full-potential calculations aimed at re-

solving the large discrepancies among the existing predictions.

Recently, one of us (J.C.B.)⁷ has generalized the linear combination of Gaussian-type orbitals–fitting function (LCGTO-FF) technique used extensively for all-electron, full-potential calculations in thin films⁸ and molecules^{9,10} to a code which treats systems with three-dimensional (3D), 2D, or 1D Block periodicity. Up to limits of computer resources, this code “GTOFF” can treat arbitrary unit cell symmetries and complexity.

For the present purpose, the key point of comparison with the LC and MM calculations (and the meaning of “all-electron, full-potential”) is that neither pseudopotentials nor muffin-tin approximations are imposed. Other than truncation of basis set expansions and approximate evaluation of functions, all of which are subject to careful determination of error limits by varying the relevant cutoffs, there are no approximations built into GTOFF which are not in the underlying LDA. Further, the code is structured to facilitate estimating the limits on precision by tuning various cutoff parameters, convergence tolerances, etc. For this study, those limits are tighter than the presumed accuracy of the LDA. GTOFF also allows comparison of distinct LDA models [here chosen to be Hedin-Lundqvist¹¹ (HL) and KSG], hence provides a reasonably sensitive test for DFT model dependencies without having to choose among the various currently competing generalized gradient approximations (whose relative reliability is still a matter of investigation).

Here we report an application of GTOFF to a 3D periodic system: calculation of the $T=0$ K static-lattice EOS for bcc, fcc, and hcp Al. We focus on the high-pressure transitions and, with two exceptions, defer detailed discussion of the low-pressure properties. The exceptions are the equilibrium lattice parameter and bulk modulus for the fcc phase. These provide a sense of the overall quality of this calculation by comparison with previous results. Using the HL LDA, we find $a_{0,\text{fcc}}=7.596$ a.u.; $B_{0,\text{fcc}}=79.7$ GPa in good agreement with Moruzzi, Janak, and Williams¹² who reported all-electron, muffin-tin, HL values of 7.59 a.u. and 80 GPa, respectively and LC’s pseudopotential, Wigner LDA values of 7.58 a.u. and 71.5 GPa, respectively.¹³ Khein, Singh, and Umrigar¹⁴ report 7.52 a.u. and 83.9 GPa (Perdew-Wang LDA); the reduced lattice constant in the latter calculation appears to be a consequence of the use of relativistic corrections. The equilibrium lattice constant we calculate also is in good agreement with the extrapolated low-temperature lattice constant for Al reported by LC, 7.60 a.u.¹³

Details of basis set selection and tabulation of exponents and contraction coefficients are left to a full paper. In summary, calculations ranged over volumes corresponding to fcc lattice constants between 5.35 and 7.80 a.u. The basis sets used were the “interior layer” basis sets developed and tested thoroughly during a recent study of Al ultrathin films.¹⁵ In the small lattice constant range, the most diffuse exponents were increased slightly when needed to avoid approximate linear dependencies. The fitting function basis sets were restricted to s -type functions since p - and d -type functions lack the correct rotational symmetry for the cubic systems.

The Brillouin zone (BZ) integrations employed uniform meshes which preserve the lattice symmetry with 72 and 76

points in the irreducible wedges of the cubic and hcp BZ’s, respectively. The BZ integrations were performed via a broadened histogram technique (with the DOS for each calculated state approximated by a normalized Gaussian with a width of 20 mRy). The accuracy of the histogram integrations was tested in a series of calculations using the linear tetrahedral method with the integrations performed over the full BZ to ensure that the correct star weights for the irreducible k points were generated.¹⁶ Fully converged results were then estimated by the extrapolation technique of Jansen and Freeman¹⁷ using BZ meshes with up to about 400 points in the irreducible wedge. Those authors had found Al to be a particularly slowly converging system with respect to BZ scan density. These calculations confirm that behavior and suggest that the linear tetrahedral integration used in the previous LCGTO work⁴ (with less than 150 irreducible k points for each structure) was not as precise as the current BZ integrations.

The EOS’s for the various phases, up to about 500 GPa, were obtained by fitting a “universal” EOS form¹⁸ to cohesive energies calculated at eight (bcc and hcp) and ten (fcc) volumes, corresponding to fcc lattice constants between 5.6 and 7.8 a.u. (The specific choice of model EOS was for reasons of utility and is not intended as a statement about the best-fit low- P EOS.) In each case, the standard deviation of the fit was less than 0.1 mRy. The transition volumes and pressures for the fcc→hcp and fcc→bcc transitions were determined from crossings of the resulting enthalpy vs pressure curves for the various structures. We find the fcc→hcp transition at 205 ± 20 GPa ($V/V_0=0.521$, with V the average volume for the transition) and the fcc→bcc transition at 340 ± 15 GPa ($V/V_0=0.446$). The error bars on the pressures are consistent with a 0.5 mRy uncertainty in the structural energy difference including both EOS fitting and BZ integration errors.

Because the calculated hcp→bcc transition lay outside the range of volumes considered in the first fit, cohesive energies were calculated at one additional volume, corresponding to an fcc lattice constant of 5.35 a.u. Repetition of the fitting procedure with this additional point included produced an hcp→bcc transition pressure of 565 ± 60 GPa ($V/V_0=0.376$). The larger error margin for this transition pressure reflects an increased standard deviation for the EOS fits, and assumes an overall uncertainty of 1.0 mRy in the relevant structural energy difference.

Comparison of the present calculated static-lattice transition pressures with the earlier predictions reveals two interesting results; see Table I. First, it is quite reassuring that the only previous all-electron, full-potential prediction⁴ for the fcc→bcc transition pressure lies within the current error bars. More importantly, the current fcc→hcp transition pressure is in good agreement with the previous intermediate prediction, namely LC’s; see the discussion above. This means that there is no obvious inconsistency between the “best” LDA prediction and the new experimental lower bound for the fcc→hcp transition pressure. In addition, the “best” LDA prediction places the transition pressure within the reach of DAC experiments.

Since the upper limit of the calculated static-lattice fcc→hcp transition pressure is barely above the lower bound determined in the recent DAC experiment, caution suggests a

TABLE I. Comparison of the present calculated static-lattice transition pressures with earlier predictions.

| Quantity | This Work | LC; Refs. 2, 13 | MJW; Ref. 12 | MM- LMTO; Ref. 1 | MM- GPT; Ref. 1 | Expt. |
|---|--------------------|--------------------|-----------------|------------------------|-----------------------|---------------------|
| $a_{0,\text{fcc}}$ a.u. | 7.596 | 7.58 | 7.59 | | | 7.60 ^a |
| B_0 GPa | 79.7 | 71.5 | 80 | | | 72.7 ^b |
| $P_{\text{fcc} \rightarrow \text{hcp}}$ GPa | 205 ± 20 | 220 | | 120 | 360 | > 220 ^b |
| V/V_0 | 0.521 | 0.50 | | | | < 0.50 ^b |
| $P_{\text{hcp} \rightarrow \text{bcc}}$ GPa | 565 ± 60 | 380 | | 200 | 560 | |
| V/V_0 | 0.376 | 0.40 | | | | |
| $P_{\text{fcc} \rightarrow \text{bcc}}$ GPa | 340 ± 15 | 300 | | | | |
| V/V_0 | 0.445 ^c | 0.45 | | | | |

^aAs cited in Lam and Cohen, Refs. 2 and 13.

^bGreene, Luo, and Ruoff, Ref. 6.

^cFor comparison, the previous LCGTO, X_α (KSG) calculation of Ref. 4 found $P_{\text{fcc} \rightarrow \text{bcc}} = 330$ GPa at $V/V_0 = 0.446$; see introductory text.

careful analysis of the current prediction. First, consider the uncertainty due to the choice of LDA model. To test for sensitivity to that choice, we recalculated $E_{\text{fcc}} - E_{\text{bcc}}$ at $a_{\text{fcc}} = 7.60$ a.u. using the KSG LDA. This modification in the LDA produced a shift of only 0.05 mRy in $E_{\text{fcc}} - E_{\text{bcc}}$ at $P = 0$. This shift should decrease rapidly as the pressure is increased, since the behavior of LDA models differs primarily in regions of low electron densities. Thus, the uncertainty in the transition pressure due to the choice of the LDA model should be negligible compared to other effects.

An important distinction between the present calculation and experiment is the neglect of phonon contributions, both zero point and thermal, in the calculation. At $P = 0$, the zero point energy for fcc Al is about 3 mRy.¹² Assuming that the zero-point energy scales as $(V/V_0)^\gamma$, with $\gamma \approx 2.2$,¹² the zero point energy of fcc Al near the fcc \rightarrow hcp transition would be on the order of 18 mRy. Even if the zero point energies for the two close-packed structures were to differ by as much as 10%, the uncertainty in the fcc-hcp structural energy differ-

ence due to neglect of the zero point motion would be no more than 1.8 mRy.

The estimated combined uncertainty in the $T = 0$ K fcc-hcp structural energy difference near the transition therefore is 2.3 mRy, 0.5 mRy from computational imprecision and 1.8 mRy from neglect of zero point motion. If the calculated enthalpy vs pressure curve for the hcp structure were to be shifted upward by a constant 2.3 mRy relative to the fcc curve, the transition pressure would be about 290 GPa. That value should represent a reasonable upper bound estimate for the 0 K fcc \rightarrow hcp transition pressure. Since this theoretical upper bound is only 70 GPa above the reported experimental lower bound, it is very likely that the recent DAC experiments came quite close to (but just short of) observing the fcc \rightarrow hcp transition. Certainly the current prediction should provide incentive for further Al EOS measurements.

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