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Density-functional calculations for cerium metal

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We present calculations of the equilibrium volume and bulk modulus for α-Ce. The calculations are based upon the local-spin-density approximation (LSDA) and the generalized-gradient approximation (GGA). These calculations are done with a full-potential linear-muffin-tin-orbital method. The equilibrium volume, which generally is too low in LSDA calculations, is improved considerably for α-Ce by the gradient correction. The increase of the equilibrium volume, when the gradient corrections are considered, results in a decrease of the bulk modulus, which therefore also becomes in better agreement with experiment. It is shown that by neglecting the nonsphericity of the electron charge density and the potential, a fortuitous improvement of the equilibrium volume and bulk modulus of α-Ce is obtained. The full-potential GGA calculations for α-Ce show an accuracy relative to experiment that is comparable to what is found for corresponding calculations for a d-transition metal. The equation of state for α-Ce is well reproduced by the full-potential GGA calculations in the pressure range for which there is data available (0–500 kbar).

Recently two independent but closely related studies of the isostructural high-density (α) and low-density (γ) fcc phases of Ce metal were published.[1,2] In these two papers, calculations using the self-interaction-corrected (SIC) local-spin-density approximation (LSDA) were compared with calculations based on the LSDA without SIC. Both these calculations were done within the atomic-sphere approximation (ASA) in which the nonspherical charge density and nonspherical potential have been neglected. Several features of the $\gamma \to \alpha$ transition in Ce were reproduced in these two studies. For instance, in agreement with experiment,[3] the SIC LSDA calculations give a localized solution for the $4f$ states and the calculated equilibrium volume agrees well with the experimental volume of γ-Ce. The experimental equilibrium volume of γ-Ce was also reproduced well in the calculation of Min *et al.*,[4] who treat the $4f$ states as part of the ion core, as well as by the subsequent study of Eriksson *et al.*,[5] who accounted for spin and orbital polarization. The LSDA calculations without SIC presented in Refs. 1 and 2 resulted in a paramagnetic, itinerant $4f$ ground state and an equilibrium volume much lower than the one obtained by SIC LSDA. This state was associated with the high density α phase. This conclusion was earlier arrived at by several authors, for instance Glötzel,[6] Skriver,[7] Min *et al.*,[4] Eriksson *et al.*,[5] and Wills *et al.*[8] Experiments demonstrate that α-Ce is a paramagnet with an equilibrium volume $\sim$ 15% lower than for γ-Ce, and the theoretical results mentioned above are in agreement with this. However, in the theoretical work for α-Ce,[1,2,4,6] the LSDA volume was substantially lower than the experimental value. The discrepancy between experiment and theory led the authors of Refs. 1 and 2, for instance, to the conclusion that their LSDA treatment of α-Ce as an itinerant $4f$ system failed to provide a correct description of this phase. Instead they suggested that this might be due to Kondo screening effects neglected in the calculations. It was stated[1] that the calculations could not discriminate between the Mott localization model[9] or the Kondo volume collapse model[10] in describing the $\gamma \to \alpha$ transition in Ce. Similarly, Svane[2] concluded that his calculations were consistent with the Mott transition model, but that the Kondo volume collapse model could not be ruled out.

In the present Brief Report we want to address the question whether there is a real need to invoke additional effects such as, for instance, the Kondo screening in order to describe the α phase of Ce accurately or whether an electronic structure calculation based upon density-functional theory is sufficient to describe the ground state of α-Ce. This paper also serves the purpose of analyzing to what extent the underestimation of the volume or the overestimation of the bulk modulus, when calculated from first principles, can be attributed to the accuracy of the computational technique.

The calculations are done for the experimental fcc structure and employ a full-potential (FP) linear-muffin-tin-orbital (LMTO) method.[11] With this approach we remove one important technical approximation used in the calculations of Refs. 1 and 2, namely, the atomic-

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sphere approximation. Hence we allow the charge density and electron potential to attain any geometrical form. Apart from the necessary approximation of the exchange-correlation energy functional, the Born-Oppenheimer approximation, and the truncation of the basis set expansion, this treatment defines an exact method. We also use a recent and successful formulation of the exchange-correlation functional, namely, the generalized gradient approximation (GGA) developed by Perdew *et al.*[12] This choice of the exchange-correlation potential is also a very important difference between our calculations and the calculations presented by Szotek *et al.*[1] and Svane.[2] The present electronic structure method has been described before,[11] but in the present context the relevant details are the following: As mentioned above, the method is a full-potential method, i.e., no spherical constraints have been applied. This is accomplished by dividing the crystal into muffin-tin spheres centered around each atomic site. These spheres do not overlap and the interstitial region between them defines about 1/3 of the total volume of the crystal. Inside the muffin-tin spheres the basis functions are defined as augmented muffin-tin orbitals with $5s$, $5p$, $6s$, $6p$, $5d$, and $4f$ partial waves. All these orbitals were defined within one energy panel, i.e., they were all allowed to hybridize. Two sets of kinetic energy parameters (double energy sets), one with an energy appropriate for the "pseudocore" states and the other with an energy suited for the valence band, have been used in the calculation. Hence we have employed an extended basis set in the reported calculations. In the interstitial region the functions are Hankel or Neuman functions depending on the sign of the kinetic energy. These functions are represented in Fourier series over the reciprocal lattice. In the case of LSDA calculations, we have used the Janak parametrization[13] of the von Barth–Hedin[14] exchange-correlation functional, whereas in the GGA calculation, the approach proposed by Perdew *et al.*[12] has been applied. The gradient terms were evaluated for the full nonspherical charge density in the muffin-tin spheres as well as in the interstitial region.[15] This treatment is necessary since neglecting these terms leads to inaccurate results.[16] The self-consistent calculations were "all electron," i.e., the core states were self-consistently calculated by solving the Dirac equation in a spherical potential. Furthermore, unlike the calculations presented in Refs. 1 and 2, the relativistic spin-orbit interaction was included in the Hamiltonian also for the valence states, in a way described by Andersen.[17] The evaluation of the gradient terms of the charge density (for the GGA calculation) requires a numerically more careful treatment, both within the muffin-tin spheres (denser mesh points) and in the interstitial region (more Fourier components), than what is usually needed in LSDA calculations. In order to compare our results with earlier data, obtained from a spherical potential (ASA), we also performed calculations for a spherical geometry of the charge density and potential [so-called muffin-tin (MT) calculations], adopting both the LSDA and GGA of the exchange-correlation potential.

In Fig. 1 we show the equation of state for α-Ce calculated with a full potential for both the LSDA and the GGA treatment of the exchange-correlation potential. Also shown in this figure are the measured room temperature data[18] and the zero pressure, low temperature data.[19] The improvement when GGA replaces LSDA for the calculated equation of state for α-Ce is apparent. Much of the discrepancy between LSDA theory and experiment has been removed in the gradient corrected calculations. The difference between experiment and theory is more pronounced for lower densities, but in fact it is similar to the difference between theory and experiment obtained for the d transition elements. In Table I the theoretical equilibrium volume for α-Ce is listed and it is about 7% smaller than the measured value, which may seem to be somewhat large, but for the $3d$ paramagnet vanadium, for instance, the discrepancy is almost the same. Therefore we conclude that the present GGA calculations describe α-Ce equally well as they describe a $3d$ transition metal.

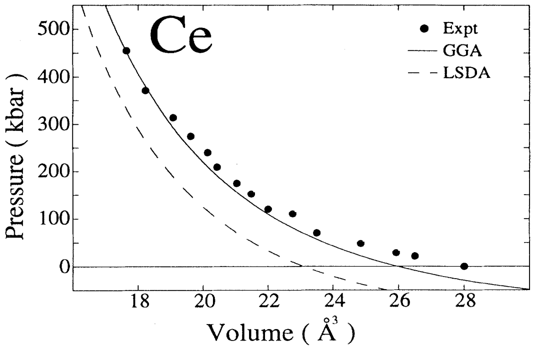

FIG. 1. Equation of state for α-Ce. The full (dashed) line represents FP GGA (FP LSDA) data. Experimental data from Refs. 18 and 19 are marked with ●.

Unfortunately the theoretical data for the atomic volume of α-Ce is very sensitive to the various approximations in the calculations and earlier theoretical efforts that are less accurate than the present one have therefore sometimes been in better and sometimes in worse agreement with experiment than the present results. For instance, the LMTO scalar relativistic calculations presented in Refs. 1 and 2, which were done in the ASA with the local-spin-density approximation, give a larger equilibrium volume (closer to experiment) than our present full-potential LSDA calculation (Table I). Therefore we find it worthwhile to demonstrate the sensitivity shown by Ce and for that reason we have studied the theoretical equilibrium volume (V_{theor}) and bulk modulus (B_{theor}, evaluated at V_{theor}) of α-Ce calculated with increasing degree of accuracy (Table II). The calculations presented in Table II are all obtained from relativistic LMTO cal-

TABLE I. Theoretical and experimental values of the equilibrium volume V and bulk modulus B for α-Ce. Experimental data are from Refs. 18 and 19.

	FP LSDA	FP GGA	Expt.
Equilibrium volume (Å^3)	22.74	26.05	28.00
Bulk modulus (kbar)	605	487	200–290

TABLE II. Relative discrepancy between theory and experiment for the equilibrium volume V and bulk modulus B (using B_{expt}=290 kbar) (Refs. 18 and 19) for α-Ce.

	MT LSDA (%)	MT GGA (%)	FP LSDA (%)	FP GGA (%)
$\frac{V_{\mathrm{theor}}-V_{\mathrm{expt}}}{V_{\mathrm{expt}}}$	−16	−4	−19	−7
$\frac{B_{\mathrm{theor}}-B_{\mathrm{expt}}}{B_{\mathrm{expt}}}$	+107	+55	+109	+68

culations. Furthermore they all include the $5s$ and $5p$ together with the $6s$, $6p$, $5d$, and $4f$ orbital states in the expansion of the one-electron wave function. This was accomplished by choosing two different sets of energy parameters for the "pseudocore" $5s$ and $5p$ and the valence states $6s$, $6p$, $5d$, and $4f$. We also allowed for a third set of energy parameters (to separate $5s$ from $5p$), but this gave only about a 1% larger equilibrium volume for α-Ce (not shown). A smaller basis set, however, where the $5s$ and $5p$ states were treated as part of the core, were found to be less appropriate since these states influence the chemical bonding in α-Ce. The total energy calculations are rather sensitive to the way in which the $5s$ and $5p$ states are treated, as pointed out by Svane.[2] However, by including these states together with the valence states in a fully hybridizing panel this problem is avoided. The least accurate calculations in Table II (MT LSDA) are done with only the spherical part of the charge density and potential in combination with the von Barth–Hedin version[13,14] of the local-spin-density approximation. This MT potential calculation should be compared to calculations in the atomic-sphere approximation (although they are not exactly equivalent calculations). The same geometrical treatment was also done for the gradient corrected potential (MT GGA). The next step is to allow for a general shape of the potential (and charge density), i.e., a FP treatment. This calculation is correspondingly called the FP LSDA. Finally, also the gradient corrected exchange correlation has been applied in combination with the general potential treatment and these calculations are denoted by FP GGA. Notice in Table II that in the MT calculation both V_{theor} and B_{theor} are closer to experiment than the corresponding FP calculations. In agreement with previous studies,[20,21] we conclude that the MT calculation tends to underestimate the chemical bonding compared to a more accurate full-potential calculation. This is seen in calculations with both the LSDA as well as the GGA for the exchange-correlation functional. Also, a larger lattice constant results in a lower bulk modulus, which for the MT calculations therefore is closer to experiment. Experimentally the bulk modulus B_{expt} is obtained from a fit to the measured equation of state and the result is very sensitive to the value of the experimental equilibrium volume V_{expt}. Theoretically the bulk modulus also shows a substantial dependence on the volume for which it is calculated and the bulk modulus evaluated (FP LSDA) at V_{expt} is 320 kbar, in very good agreement with experiment. It is also interesting to notice that the MT GGA result is fortuitously in very good agreement with experiment. Consistent with previous studies, we conclude that the nonspherical part of the gradient corrected potential is very important.[16] As noted above, the most accurate treatment (FP GGA) gives quite good agreement with experiment, whereas the FP LSDA treatment is less satisfactory. This observation was also made in calculations for the actinide analog to α-Ce, namely, Th metal. For this element the FP LSDA equilibrium volume is too low compared to experiment, whereas the FP GGA equilibrium volume agrees better (and is 10% lower than experiment).[22] To summarize the results in Table II we note that improving on the calculational technique and considering a general shape of the density and potential makes the agreement between experiment and theory worse for both the LDA and the GGA calculations. Also, the GGA equilibrium volumes are consistently larger and in better agreement with experiment.

In connection to investigating the sensitivity of the equilibrium volume and bulk modulus on the various approximations made in the calculations, we find it interesting to compare our results with previous theories. Drastically different values for the equilibrium volume can for instance be obtained in LMTO ASA (LSDA) calculations, depending on how the $5p$ states are treated. In the work of Refs. 1, 2, 4, and 6, the $5p$ states were treated as band states and the equilibrium volume was found to be ~ 26.0, 25.7, 23.3, and 24.4 Å^3, respectively. In Ref. 5 the $5p$ states were treated as core states and this gave fortuitously an equilibrium volume in better agreement with experiment. The values of Refs. 1, 2, 4, and 6 should be compared to our MT LSDA result, which is 23.5 Å^3. Our value compares better with Refs. 4 and 6 than with Refs. 1 and 2. The calculations of Refs. 1, 2, 4, and 6 are based on the same method and treat the same Hamiltonian and should therefore give similar equilibrium volumes. Further, our FP LSDA equilibrium volume compares quite well with the FP LSDA value of Ref. 4. This is quite encouraging since it means that two different full-potential, energy band methods give similar results. The small difference between them is due to that we presently treat the spin-orbit coupling, which was not the case in Ref. 4. If we calculate the equilibrium volume without the spin-orbit coupling in the Hamiltonian, we obtain in fact the same value as in Ref. 4. Moreover, differences in convergence in the basis functions may give slightly different results. Also, the equilibrium volume of Ref. 8 is larger than the present one due to that we here are using a better converged basis set (double basis).

To conclude, careful analysis of different numerical approximations show that both V_{theor} and B_{theor} of α-Ce are very sensitive to the computational method. In fact, the theoretically least accurate calculation (MT GGA) gives the best results, whereas the FP LSDA calculation gives the worst agreement with experiment. However, it is also found that the most accurate calculation (FP GGA) agrees quite well with the experimental equation of state and that the remaining discrepancy is of the same size as is found, for example, for a nonmagnetic d metal (V). Hence, from our present results we cannot support the view expressed in Refs. 1 and 2 that α-Ce should be treated differently from other (itinerant) f or d metals. We have demonstrated that for α-Ce the calculated results are very sensitive to the approximations used, such as the ASA and the LSDA. This fact may have led to a confusion about whether or not there exist real physical effects, such as the proposed Kondo screening,[1,2] that cannot be accounted for straightforwardly in an electronic structure calculation based upon density-functional theory. We further point out that the version of the generalized gradient approximation[12] we have used in the present calculations might need to be improved upon since the exchange-correlation treatment still seems to have a tendency to overestimate the chemical bonding in *f* metals (i.e., not only α-Ce).[22] Finally, one may also question somewhat the accuracy of the experimental data for α-Ce. For instance, for the equilibrium volume of α-Ce, data spanning from 28.0 to 29.1 Å^3 (Refs. 19 and 23) have been reported. Consequently, the value of the measured bulk modulus might also have a large error bar and in fact the elastic constants (C_{11}, C_{12}, and C_{44}) have not yet been obtained experimentally for α-Ce. The difficulty in analyzing experimental data for Ce in the α phase may be explained by the difficulties in preparing a sample of pure α-Ce without any mixing of the β phase of cerium.[24] We conclude that the present result, combined with the results obtained in Refs. 1, 2 and 4–8 supports the Mott transition picture of the $\gamma \rightarrow \alpha$ phase transformation in Ce metal.

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