PHYSICAL REVIEW B VOLUME 56, NUMBER 12 15 SEPTEMBER 1997-II

Electronic-structure calculations of praseodymium metal by means of modified density-functional theory

A. Svane
Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

J. Trygg and B. Johansson
Condensed Matter Theory Group, Department of Physics, University of Uppsala, Box 530, Uppsala, Sweden

O. Eriksson
Condensed Matter Theory Group, Department of Physics, University of Uppsala, Box 530, Uppsala, Sweden
and Center for Materials Science and Theoretical Division, Los Alamos National Laboratory,
Los Alamos, New Mexico 87544

(Received 10 February 1997)

Electronic-structure calculations of elemental praseodymium are presented. Several approximations are used to describe the Pr f electrons. It is found that the low-pressure, trivalent phase is well described using either the self-interaction corrected (SIC) local-spin-density (LSD) approximation or the generalized-gradient approximation (GGA) with spin and orbital polarization (OP). In the SIC-LSD approach the Pr f electrons are treated explicitly as localized with a localization energy given by the self-interaction of the f orbital. In the GGA+OP scheme the f-electron localization is described by the onset of spin and orbital polarization, the energetics of which is described by spin-moment formation energy and a term proportional to the total orbital moment, L_z^2. The high-pressure phase is well described with the f electrons treated as band electrons, in either the LSD or the GGA approximations, of which the latter describes more accurately the experimental equation of state. The calculated pressure of the transition from localized to delocalized behavior is 280 kbar in the SIC-LSD approximation and 156 kbar in the GGA+OP approach, both comparing favorably with the experimentally observed transition pressure of 210 kbar. [S0163-1829(97)01136-3]

I. INTRODUCTION

The series of lanthanide and actinide metals exhibit a rich variety of structural phase transitions as a function of external pressure.[1,2] In the pressure range 0–150 kbar, the sequence of hexagonal close-packed (hcp) structure → Sm structure → double hexagonal close-packed (dhcp) structure → face-centred cubic (fcc) structure → distorted fcc structure generally is observed,[2,3] and understood in terms of a transfer of valence electrons from sp into d character.[4] At higher pressures, volume collapse transitions are sometimes observed for the earlier lanthanides and medium-heavy actinides and attributed to the sudden delocalization of f electrons with associated increase in chemical binding.[5–10]

Praseodymium metal falls into this general pattern. At ambient conditions Pr attains the dhcp structure, but at a pressure around 40 kbar a structural phase transition to the fcc structure is observed, and at still higher pressures ($\sim$62 kbar) a distorted fcc structure is seen.[8] These low-pressure phases are all characterized by relatively high symmetry and/or quite good packing ratios and no particular volume collapse is associated with the phase transitions. It is believed that the f electrons are localized in these phases, which, for example, is corroborated by the fact that Y (being trivalent but having no f electrons) exhibits the same sequence of structures as the lanthanides and the heavier actinides.[2] In contrast, at $P\sim 210$ kbar Pr is observed to undergo yet another structural phase transition to the α-uranium (α-U) structure accompanied by a 9–10 % volume collapse.[6–9] The α-U structure is thought to be associated with itinerant f-electron behavior, for which reason this phase transition is believed to mark the onset of f-electron delocalization. Thus the crystallographic transition is likely to be driven by a simultaneous electronic phase transition.

Theoretical work using band structure calculations based on the local-spin-density (LSD) approximation to density-functional theory has confirmed that in order to reproduce the experimental equilibrium volume the f electrons should not be treated as bandlike, but rather be kept as frozen core electrons.[11,12] If itinerant f electrons are allowed for in the calculations they contribute such large extra cohesion as to produce much too low equilibrium volumes. The LSD ground state of the lanthanide metals calculated in this way is qualitatively wrong, due to the fact that the formalism does not generally allow for a possible energy gain by localization. The generalized gradient approximation (GGA) does not alter the situation, although the volumes of the itinerant phases are improved in comparison with LSD.[13]

Recent developments in electronic structure schemes using orbital polarization[14] (OP) and self-interaction corrections[15,16] (SIC) have provided frameworks for the description of the transition from localized to delocalized behavior of the f electrons. In the orbital polarization scheme the f electrons are treated as band states, but a term is added to the total energy functional to improve the description of the intra-atomic interaction energies. This term lowers the energy of one-electron states of a given spin and with a large

m_l quantum number, thus facilitating the formation of significant spin and orbital moments. At large volumes, when f-electron states have little overlap with their neighbors, a complete spin and orbital polarization is favorable, and as a consequence of the filled f subbands the f electrons do not contribute to the cohesion. Upon compression, the increased f-electron hopping matrix elements favor band formation and the orbital polarization decreases gradually until eventually the f electrons exhibit full itinerant behavior. In application to Ce (Ref. 14) a Maxwell type instability loop was observed in the calculated pressure-volume curve giving rise to a first-order transition from localized to delocalized f-electron behavior. The calculated transition takes place at a somewhat too negative pressure compared to the experimentally observed $\gamma \rightarrow \alpha$ transition. When the same theory is applied to Pr, a similar decrease of the orbital moment is observed at a volume corresponding to the experimental volume of the localization-delocalization transition, however, not with a Maxwell loop in the pressure-volume relation. The orbital polarization scheme has been very successful in describing the orbital moment formation in systems like uranium compounds[17] as well as the magnetocrystalline anisotropy of 3d metals,[18] where the f and d electrons, although correlated, are best described as delocalized.

In the self-interaction corrected LSD formalism[19,20] (SIC-LSD) the energy of a localized f electron is corrected for the spurious self-interaction inherent in the LSD formalism. This provides an energy functional, which may be minimized either by a set of delocalized Bloch states or by a set of states of which at least some are localized, i.e., of non-Bloch form. By comparing the two competing minima of the SIC-LSD total energy functional one may discuss the two sides of the localized-delocalized transition. Applied to Ce (Refs. 15, 16, and 20) the SIC-LSD scheme has been very successful in describing the $\gamma \rightarrow \alpha$ phase transition, even at finite temperature. The SIC-LSD approach has recently been applied to Pr (Ref. 21) at the experimental lattice constant and was found to improve the description of the Fermi surface of Pr. In this study the drastic improvement of the SIC-LSD approach compared to the LSD was due to the fact that the occupied Pr f states are removed from the Fermi level.

In comparison to the orbital polarization scheme the moment formation energy of an f electron in Ce is ~ 2 times larger in SIC-LSD (~ -64 mRy in SIC-LSD compared to ~ -30 mRy in the orbital polarization scheme). These moment formation energies do not represent the total energy change when a system undergoes a delocalization-localization transition, since the loss in band formation energy is a balancing contribution. The fact that the localization-delocalization transition pressure is somewhat too low in the orbital polarization scheme (~ -50 kbar) (Ref. 14) but about right in the SIC-LSD theory (~ -7 kbar) (Refs. 15, 16, and 20) suggests that for Ce the magnitude of the localization energy in the latter scheme is essentially correct. The functional dependence of the localization energy on the number of f electrons is quite different in the two schemes, being approximately linear in SIC-LSD and scaling like the sum of the square of the spin and orbital angular momentum in the orbital polarization energy. A third calculational scheme often used to describe orbital polarization and localization effects is the LDA+U theory,[22] where a Hubbard-like term is added to the LSD Hamiltonian. This scheme has been applied successfully to well-localized systems like NiO (Ref. 23) and KCuF_3,[24] but in view of the large value of the added term it will overestimate the tendency to localization, i.e., it is only applicable to well-localized systems but less appropriate for systems on the borderline. There is some uncertainty in determining the compensating term in the LDA+U energy functional, so the localization energy for a Ce f electron in this scheme is not easy to assess. The LDA+U calculations of Ref. 25 showed that a U value of 5–6 eV is appropriate for Ce, if a local moment shall be formed at the γ-phase volume but not at the α-phase volume. This is also the U value generally accepted from photoemission experiments.[26] However, Sandalov *et al.*[27] elaborated on this and found that in a more realistic implementation a localization of the f states was found at a lower value of the Hubbard U, ~ 3 eV. If one believes that the α phase of Ce has delocalized f states one must conclude that the LDA+U overestimates the tendency to localization. Although it has not been investigated in detail it is likely that within the LDA+U approach the 4f states of Ce are essentially localized up to several hundred kilobars.

In the present work we have undertaken the investigation of the structural phase transition of Pr, observed to occur at 210 kbar, using the SIC-LSD and orbital polarization schemes and find that both schemes are adequate for the low-pressure localized phase, while the high-pressure delocalized phase is best described with the GGA. In Sec. II the SIC-LSD and OP schemes are briefly described, while Sec. III presents the results of our calculations together with a discussion.

II. DETAILS OF CALCULATIONS

In the SIC-LSD approximation[19,20] one subtracts from the LSD total energy functional the self-Coulomb and self-exchange-correlation energy for each occupied electron state:

$$E^{\mathrm{SIC}}[\{\psi_\alpha\}] = \sum_\alpha \langle \psi_\alpha | -\Delta | \psi_\alpha \rangle + U[n] + E_{\mathrm{xc}}^{\mathrm{LSD}}[\overline{n}] + V_{\mathrm{ext}}[n] - \sum_\alpha \delta_\alpha, \qquad (1)$$

where

$$\delta_\alpha = U[n_\alpha] + E_{\mathrm{xc}}^{\mathrm{LSD}}[\overline{n}_\alpha]. \qquad (2)$$

Here, E^{SIC} is written as a functional of a set of N occupied orthonormal single-electron wave functions ψ_α. $\overline{n}$ is the total spin density of the system, $\overline{n}(\mathbf{r}) = (n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}))$, $n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r})$, and $\overline{n}_\alpha$ is the spin density of the αth state. $U[n]$ and $E_{\mathrm{xc}}^{\mathrm{LSD}}[\overline{n}]$ are the Coulomb and the exchange-correlation energies of the electron gas, respectively, while $V_{\mathrm{ext}}[n]$ denotes the interaction energy with the lattice of ions.

The last term in Eq. (1) represents the self-interaction correction, where for each occupied orbital ψ_α the Coulomb and exchange-correlation energies of the corresponding spin density $\overline{n}_\alpha$ are subtracted. As written in Eq. (1), E^{SIC} appears to be a functional of the set of occupied orbitals rather than of the total spin density only, like E^{LSD}. By a reformulation it may be shown[19,28] that E^{SIC} can in fact be regarded as a functional of the total spin density only. In periodic solids the SIC-LSD constitutes an extension of LSD in the sense that the set of Kohn-Sham orbitals which minimize E^{LSD} also provide a local minimum of E^{SIC}.[29] The question is whether a set of single-particle states, not all of Bloch form, exists such that E^{SIC} has a lower energy when evaluated with these orbitals. When this occurs, the self-consistent value of the self-interaction represents the localization energy for that particular orbital, which has to be balanced by the loss of band formation energy. For the actual implementation of the minimization of the SIC-LSD energy functional the reader is referred to Ref. 20. The details of the present calculations were identical to those used for Ce in Ref. 20. In particular, the electron eigenstates were expanded in a double tight-binding linear-muffin-tin orbitals (LMTO) basis set.[30] In this way the $5s$ and $5p$ semicore states of Pr as well as $6s$ and $6p$ hybridization may be described. In addition, the atomic sphere approximation (ASA) was applied for the SIC-LSD calculations, i.e., the crystal volume is divided into slightly overlapping atom-centered spheres, inside which the potential is taken spherically symmetric. The full-potential LMTO method,[31,32] which does not invoke this approximation, was applied for the α-U structure and for the calculations using the GGA to the exchange-correlation energy.

In the orbital polarization scheme,[14] a term

$$E_{\mathrm{OP}}=-\frac{1}{2}E^3L_z^2 \qquad (3)$$

is added to the LSD total energy functional. Here, E^3 is the Racah parameter, related to the well-known Slater integrals F_k:[33]

$$E^3=(5F_2+6F_4-91F_6)/3, \qquad (4)$$

while L_z is the z component of the total angular momentum. The origin of the OP energy is from simple considerations over the electrostatic and exchange energies of the various terms of incompletely filled shells in the Hartree-Fock approximation, where it is observed that the lowest multiplet (i.e., maximal S and L, according to Hund's first two rules) of a given configuration (f^n) is lower than the mean energy of that configuration, the Grand Bary Center, by approximately E_{OP}.[33,34] Therefore the rationale of introducing the OP energy correction is that this atomic term energy difference is not represented by standard LSD or GGA calculations. In analogy with Stoner theory of spin magnetism,[35] where a term $-\frac{1}{4}IS_z^2$ describes the extra exchange energy associated with spin polarization, the energy functional of the orbital polarization is $-\frac{1}{2}E^3L_z^2$. The spin magnetic interaction energy is of course inherent in the LSD energy functional.[35] In the OP scheme the onset of localization is signaled by the formation of a large spin and orbital moment, when the intra-atomic interaction energies (in this case the spin polarization and E_{OP} terms) dominate over the inter-atomic interactions (i.e., the hopping integrals), leading to one or several levels being pulled below the Fermi level, and consequently becoming completely filled. These levels then represent a localized situation, since for filled bands a Bloch and Wannier representation are equivalent. A similar reasoning has been used in previous studies of systems with half filled shells, where the onset of spin polarization represents the onset of localization.[36] In the two theoretical methods used in the present paper localization is described in the same way, although at first sight the mechanisms for driving localization seem somewhat different. The common signature of localization in the SIC-LSD and OP schemes is the occurrence of one or several narrow electron states, which are completely filled and drawn away from the Fermi level.

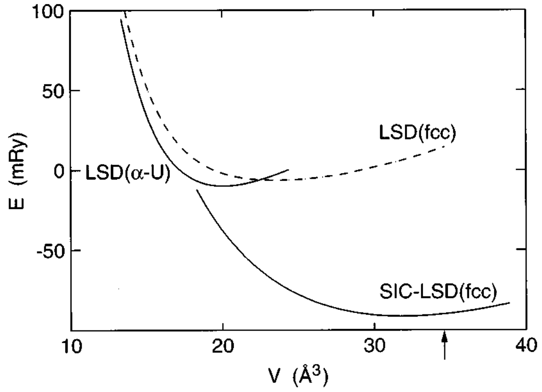

FIG. 1. Total energy of praseodymium (in mRy/atom, with an arbitrary energy offset) as a function of atomic volume (in Å^3). The curve marked SIC-LSD(fcc) corresponds to the calculation in the fcc structure with two localized f electrons per atom, while the curves marked LSD(fcc) and LSD(α-U) correspond to itinerant f electrons, in the fcc and α-U structures. The arrow indicates the position of the experimental equilibrium volume.

III. RESULTS

In Figs. 1 and 2 the calculated total energy of praseodymium is shown as a function of atomic volume. In Fig. 1 two curves show the positions of the two local minima of the SIC-LSD energy functional in the fcc structure, which correspond to localized or delocalized f electrons, respectively. In the latter case, the SIC-LSD approximation is identical to the LSD approximation. The third curve in Fig. 1 represents the energy of Pr calculated in the α-U structure with the LSD approximation, i.e., also with the f electrons treated as delo-

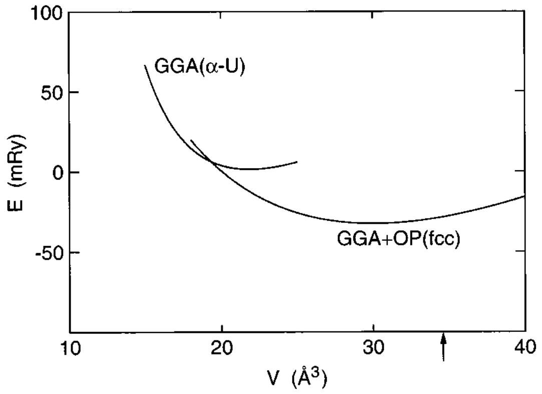

FIG. 2. Same as Fig. 1 but with the GGA and GGA+OP approach.

calized. Due to the relatively low symmetry of the α-U structure, the total energy of this phase cannot be accurately calculated within the ASA. Therefore the α-U curve of Fig. 1 was produced by calculating the total energy difference between the α-U structure and the fcc structure with the full potential LMTO method,[31] and adding this quantity to the fcc LSD total energy as calculated in the ASA.

The lowest total energy is found for the SIC-LSD curve, i.e., when the f electrons are treated as localized and self-interaction corrected. The equilibrium volume is $V_0^{\rm theor}=32.0$ Å^3, which should be compared to the experimental value $V_0^{\rm expt}=34.6$ Å^3.[37] The magnitude of the self-interaction correction at the eqilibrium volume is $\delta_\alpha=65$ mRy [cf. Eq.(1)] per f electron, so that the localization energy gain is -130 mRy per Pr atom. This gain is counteracted by the loss of band formation energy, $+12$ mRy per atom, so that the net energy difference between the SIC-LSD and the LSD minima at the eqilibrium volume is -118 mRy per atom. The theoretical bulk modulus is $B_0^{\rm theor}=289$ kbar, which compares favorably with the experimental value of $B_0^{\rm exp}=306$ kbar.[38] The pressure derivative of the bulk modulus is $B_0'^{\rm theor}=2.8$. In the present study we ignore the actual dhcp ground state structure of Pr at ambient pressure, since our main focus is on the large volume collapse localization-delocalization transition. The total energy versus volume curves of the trivalent dhcp, fcc, and distorted fcc phases are bound to lie very close, since the volume changes on transitions are rather small, so we have chosen them to be represented by the single fcc total energy curve of Fig. 1.

For the dense phase it is seen that the α-U structure is considerably more favorable than the fcc phase when the f electrons are considered to be itinerant, in accord with the fact that this structure often appears in itinerant f-electron metals. As recently explained,[39] this originates from a symmetry breaking (Jahn-Teller/Peierls-like) mechanism, where electron states which are degenerate in the high symmetry phase may become nondegenerate in a crystal with lower symmetry. One or several of the degenerate states are then lowered whereas others are raised in energy. If the states being raised in energy end up above the Fermi level, the system will gain energy from the bands which are lowered and lose no energy from the states which have moved above the Fermi level, i.e., a net energy gain is achieved. It was demonstrated that this mechanism is operational in all metals with narrow bands in the vicinity of the Fermi level, be it itinerant f-electron systems or normal *spd* metals at artificially expanded lattice constants.[39]

The parameters of Pr in the α-U structure were taken to be equal to those of U, i.e., neither the b/a and c/a ratios nor the internal displacement parameter were optimized. The structural parameters, b/a and c/a, derived experimentally for Pr (Ref. 7) do not differ substantially from those of U used here. Such an optimization is feasible but computationally demanding. It will lead to a total energy curve for the dense phase, which lies somewhat lower than the curve in Fig. 1, but the energy gain on optimization is modest compared to the α-U–fcc energy difference.

Recently, it was demonstrated that the GGA substantially improves the equilibrium volume in f-electron systems,[13] including the α phase of Ce, and one may hope that a better description of the collapsed phase of Pr may also be achieved within the GGA. To investigate this we calculated the total energy of Pr with the GGA, as shown in Fig. 2. In this figure the localized phase of Pr is described with the OP, which quite similarly to the SIC-LSD approach leads to a zero-pressure volume of 30.0 Å^3. The equation of state of the α-U structure is considerably improved by the GGA functional, as will be discussed below and may be seen, for instance, by the fact that the minimum of the total energy curve for the α-U structure is found at almost 10% larger volume (at 21.8 Å^3, instead of 20.0 Å^3).

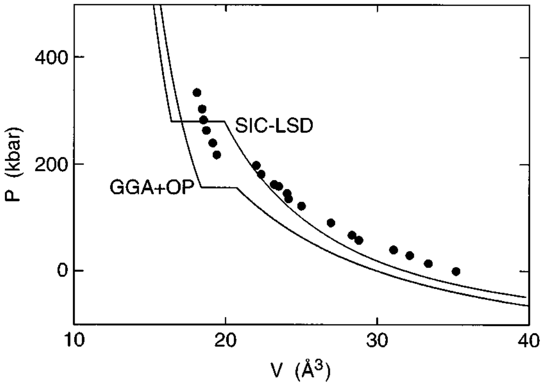

FIG. 3. Equation of state of praseodymium, based on the calculations of Figs. 1 and 2. The volume is in Å^3, and the pressure in kbar. Experimental data from Ref. [9] are marked with •.

The common tangents in Figs. 1 and 2 define the transition pressure from localized to delocalized f-electron behavior, which is calculated to be $P_1^{\rm theor}=280$ kbar in the SIC-LSD calculation of Fig. 1 and $P_2^{\rm theor}=156$ kbar in the GGA+OP calculation of Fig. 2. The experimental transition pressure is $P^{\rm expt}=210$ kbar. The high and low volumes on each side of the transition are in the SIC-LSD approach $V_{1h}^{\rm theor}=19.9$ Å^3 and $V_{1l}^{\rm theor}=16.4$ Å^3, corresponding to a 17.6% volume collapse and in the GGA+OP approach $V_{2h}^{\rm theor}=20.7$ Å^3 and $V_{2l}^{\rm theor}=18.4$ Å^3, corresponding to an 11% volume collapse. Experimentally, the same quantities are $V_h^{\rm expt}=21.7$ Å^3 and $V_l^{\rm expt}=19.7$ Å^3 with a volume collapse of 9.3%.[9]

The calculated pressure-volume curves from the SIC-LSD and OP-GGA approximations are shown in Fig. 3 and compared to experimental data.[9] From Fig. 3 it is seen that the SIC-LSD formalism provides a fairly accurate description of the low-pressure phase of praseodymium, while the high-pressure α-U phase is less accurately described, but greatly improved by the GGA. In the SIC-LSD approach the qualitative features of the localization-delocalization transition are thus reproduced, but the transition pressure is too large, and the volume collapse is almost twice as large as observed experimentally.

In the GGA+OP approach the transition pressure is too low, and the volume for which the transition occurs is also somewhat too low. However, the volume collapse is about correct. The difference from the SIC-LSD results is partly due to the larger volume of the α-U structure in the GGA and partly due to a lower localization energy compared to the SIC-LSD approach. In the SIC-LSD approach the moment formation energy is 118 mRy as compared to 80 mRy in the

GGA+OP scheme. When inspecting the $4f$ localized phase we note that the SIC-LSD approach reproduces the experimental equation of state slightly better than the GGA+OP theory.

IV. CONCLUSIONS

In summary, we have reproduced the observed transition in elemental praseodymium from a low-pressure close-packed phase to a more open high-pressure structure. We explain this phenomenon as due to a localization-delocalization transition of the $4f$ electrons, where at sufficiently large $4f$ wave function overlap the kinetic energy gained in the band formation becomes larger than the local-moment formation energy. This conclusion was reached by means of two different, commonly used approaches for correcting LDA theory in describing localization-delocalization transitions. The two approaches seem at first sight quite different in nature but yield the same qualitative results, with a decent description of the observed volume collapse of Pr metal. The volume collapse is in both theories explained as due to an onset of delocalized $4f$-electron behavior. There are some differences in the quantitative results from the two theoretical schemes, as is also the case in Ce metal. However, one conclusion to be drawn from this study is that both theoretical approaches describe the localized phase as having a set of levels at low energy, away from the Fermi level. The location of these levels is quite different in the two approaches. However, this energy is not a very meaningful quantity in any case—rather the kinetic, potential, and exchange and correlation energies are the important factors. These terms are very similar in the two approaches, which may be seen from the moment formation energy which differs by some 40 mRy. In the volume interval where the transition occurs a shift of the total energy curve by this amount does not have a dramatic influence on the qualitative interpretations, but may cause the discrepancies in the calculated transition pressures.

The origin of the OP correction is intimately connected to the different angular behavior of the different (l,m_l) orbital states, and from this it follows that the Coulomb and exchange energy is minimized for a population of states which is given by Hund's rules. This mechanism should be possible to capture also in a SIC formalism if it could be applied to a potential with full angular behavior. Such a theory which both accounts for the atomic multiplet energy and describes properly the Hubbard-like Coulomb correlations would clearly be an extension of this work. This could possibly account for the remaining discrepancies between theory and experiment.

ACKNOWLEDGMENTS

B.J. and O.E. are grateful for support from the Swedish Natural Science Research Council and from the materials consortium no. 9. A.S. acknowledges support from the Danish Natural Science Research Council, Grant No. 11-0694-1.

---

[1] A. K. McMahan, J. Less-Common Met. **149**, 1 (1989).

[2] U. Benedict, W. A. Grosshans, and W. B. Holzapfel, Physica B & C **144B**, 14 (1986).

[3] B. Johansson and A. Rosengren, Phys. Rev. B **11**, 2836 (1975).

[4] J. C. Duthie and D. G. Pettifor, Phys. Rev. Lett. **38**, 564 (1977); A. K. McMahan, H. L. Skriver, and B. Johansson, Phys. Rev. B **23**, 5016 (1981).

[5] B. Johansson, Philos. Mag. **30**, 469 (1974).

[6] H. K. Mao, R. M. Hazen, P. M. Bell, and J. Wittig, J. Appl. Phys. **52**, 4572 (1981).

[7] G. S. Smith and J. Akella, J. Appl. Phys. **53**, 9212 (1982).

[8] W. A. Grosshans, Y. K. Vohra, and W. B. Holzapfel, J. Phys. F **13**, L147 (1983).

[9] W. A. Grosshans and W. B. Holzapfel, J. Phys. (Paris) Colloq., Suppl. **45**, C8-141 (1984).

[10] Y. Vohra, J. Akella, S. Weir, and G. Smith, Phys. Lett. A **158**, 89 (1991); P. Söderlind, O. Eriksson, J. M. Wills, and B. Johansson, Phys. Rev. B **48**, 9212 (1993).

[11] B. I. Min, H. J. F. Jansen, T. Oguchi, and A. J. Freeman, J. Magn. Magn. Mater. **61**, 139 (1986).

[12] H. L. Skriver, Europhys. Lett. **7**, 629 (1988).

[13] P. Söderlind, O. Eriksson, B. Johansson, and J. M. Wills, Phys. Rev. B **50**, 7291 (1994); **52**, 13 169 (1995).

[14] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 7311 (1990).

[15] Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. Lett. **72**, 1244 (1994).

[16] A. Svane, Phys. Rev. Lett. **72**, 1248 (1994).

[17] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 9087 (1990); L. Sandratskii and J. Kübler, Phys. Rev. Lett. **75**, 946 (1996).

[18] J. Trygg, B. Johansson, O. Eriksson, and J. M. Wills, Phys. Rev. Lett. **75**, 2871 (1995).

[19] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[20] A. Svane, Phys. Rev. B **53**, 4275 (1996).

[21] W. M. Temmerman, Z. Szotek, and H. Winter, Phys. Rev. B **47**, 1184 (1993).

[22] B. Brandow, Adv. Phys. **26**, 651 (1977). The LDA+U theory of Brandow was independently implemented by Refs. 23 and 25.

[23] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[24] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).

[25] A. M. Boring, R. C. Albers, O. Eriksson, and D. D. Koelling, Phys. Rev. Lett. **68**, 2652 (1992).

[26] L. Z. Liu, J. W. Allen, O. Gunnarsson, N. E. Christensen, and O. K. Andersen, Phys. Rev. B **45**, 8934 (1992).

[27] I. Sandalov, O. Hjortstam, B. Johansson, and O. Eriksson, Phys. Rev. B **51**, 13 987 (1995).

[28] A. Svane, *ibid.* **51**, 7924 (1995).

[29] The LSD solution is readily seen to constitute a saddle point for the SIC-LSD energy functional, since the self-interaction correction in Eq. (1) is zero for Bloch-like states. However, adding an infinitesimal non-Bloch component to any of the LSD eigenfunctions leads to a *positive* self-interaction correction, since the exchange-correlation term dominates [last term in Eq. (2)]. Spe-

cifically, for λ small, $U[\lambda n]\sim\lambda^2 U[n]$, but $E_{xc}[\lambda \overline{n}]\sim\lambda^{4/3}E_{xc}[\overline{n}]$. Hence the LSD is actually a local minimum.

[30] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984); O. K. Andersen, O. Jepsen and O. Glötzel, in *Canonical Description of the Band Structures of Metals*, Proceedings of the International School of Physics, Course LXXXIX, Varenna, 1985, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985), p. 59.

[31] J. M. Wills (unpublished).

[32] J. Trygg, Ph.D. thesis, Uppsala University, 1995.

[33] C. K. Jørgensen, *Orbitals in Atoms and Molecules* (Academic, London, 1962).

[34] L. J. Nugent, J. Inorg. Nucl. Chem. **32**, 3485 (1970).

[35] J. Kübler and V. Eyert, in *Electronic and Magnetic Properties of Metals and Ceramics*, edited by K. H. J. Buschow (VCH, Weinheim, 1994), Vol. 3A, p. 1.

[36] H. L. Skriver, O. K. Andersen, and B. Johansson, Phys. Rev. Lett. **44**, 1230 (1980).

[37] B. J. Beaudry and P. E. Palmer, J. Less-Common Met. **34**, 225 (1974).

[38] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (John Wiley & Sons, New York, 1976).

[39] P. Söderlind, O. Eriksson, B. Johansson, J. M. Wills, and A. M. Boring, Nature (London) **374**, 524 (1995).