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Electronic and structural properties of Lu under pressure: Relation to structural phases of the rare-earth metals

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Ground-state electronic and structural properties of Lu under pressure are investigated with use of the self-consistent all-electron total-energy linear muffin-tin orbital band-structure method within a local-density-functional approximation. Pressure-induced structural transitions are found to occur in the following sequence: hcp—(Sm-type)—dhcp—fcc, which is the same as that observed in the crystal structures of the trivalent rare-earth metals with decreasing atomic number. This structural transition is correlated with the increase in the number of d electrons under pressure.

I. INTRODUCTION

The element Lu ($Z=71$), located at the end of rare-earth series; in its metallic state it has the highest density among the rare-earth metals. Its fourteen f electrons establish a completely filled f shell and the remaining three conduction electrons are considered to determine the electronic and magnetic properties of Lu in a manner similar to those of the d-band transition metals.

The stable crystal structure of Lu at normal pressure is hcp as is also found for the other heavy trivalent rare-earth materials (Gd to Tm). A structural transition from this stable hcp to the Sm-type structure was observed[1] in high-pressure ($P\sim230$ kbar) x-ray diffraction experiments. This structural transition points out an interesting mechanism which might be operating and which also plays a role to explain the crystal structure sequence observed in the trivalent rare-earth series. A sequence of close-packed structures, hcp—(Sm-type)—dhcp—fcc, is observed with decreasing atomic number in the trivalent rare-earth series. There have been many conjectures[2] to account for this phenomenon. Duthie and Pettifor[3] found a close relationship between the crystal structure and the occupancy of the 5d band, using a canonical band-structure method within the atomic sphere approximation. In their work, the d-band occupancy, N_d, increases monotonically from right to left in the trivalent rare-earth series and determines the stable structure. This mechanism is similar to that which occurs in the d-band transition metals,[4] where a hcp-bcc-hcp-fcc structural sequence is found as the d band occupancy increases. (At this point, it is important to note that the f electrons in the rare earths are believed to be completely localized and to play no significant role in determining the crystal structure.) These concepts were extended by Skriver[5] to obtain the stable structures under pressure in Lu and La based on a comparison of one-electron eigenvalue sums for different structures. He found a pressure induced structural transition in Lu and La corresponding to the crystal structures which appear in the rare-earth series. Unfortunately, Skriver obtained for Lu at ambient pressure, the stable Sm-type structure rather than the observed hcp structure.

The first electronic band-structure calculation for Lu was carried out by Dimmock *et al.*[6] using the nonrelativistic augmented-plane-wave (APW) method and later work was performed by Keeton and Loucks[7] using the relativistic APW method. Neither of these early calculations were self-consistent and the potentials were constructed from a Hartree-Fock-Slater (HFS) calculation with an assumed atomic configuration ($4f^{14}5d^{1}6s^{2}$). These early results showed that Lu has a band structure which is typical for a transition metal; the 4f band is situated below the bottom of conduction band. In keeping with the localized nature of the 4f electrons, the location of the 4f band was found to be very sensitive to the choice of the potential. More recently, self-consistent APW calculations were performed by Tibbetts and Harmon[8] and by Harima *et al.*[9] in which the f electrons are treated as valence bands. Tibbetts and Harmon[8] investigated the Fermi-surface properties whereas Harima *et al.*[9] studied the f-band position for hcp Lu at the experimental lattice constant.

In this work, we investigate the ground-state electronic and structural properties of Lu with an all-electron, total energy, band-structure approach. We use the self-consistent fully relativistic[10] and semirelativistic[11] versions of the linear-muffin-tin-orbital (LMTO) method[12] within the local-density-functional approximation[13] (LDA) for our study of the electronic band structure. The interpolation formula of Hedin and Lundqvist[14] is used for the exchange-correlation potential. The resulting ground-state electronic structures of Lu are given in Sec. II. Pressure-induced structural transitions are investigated in Sec. III and a discussion and a summary are presented in Sec. IV.

II. ELECTRONIC STRUCTURE

We have performed self-consistent band-structure calculations for trivalent Lu metal using the LMTO method. The fully relativistic band structure of hcp Lu at the experimental lattice constant ($r_{WS}=3.62$ a.u.; the Wigner-Seitz radius, r_{WS}, is used hereafter as a measure of the lattice constant) is plotted in Fig. 1. The $4f$ electrons are treated on the same footing as the other valence electrons in this calculation. (In another set of calculations, the $4f$ electrons are treated as core.) The general shape of the band structure is similar to the pioneering non-self-consistent band-structure calculations,[6,7] except for the location of the $4f$ bands.

Two very narrow $4f$ bands ($4f_{5/2}$ and $4f_{7/2}$) lie in the middle of the conduction bands, about 5.4 and 4.0 eV below the Fermi level (E_F), respectively, and are separated by 1.4 eV due to the spin-orbit interaction. These results are consistent with those by Harima *et al.*,[9] who obtained the $4f$-level position, 4.9 eV below E_F, using the semirelativistic APW band method. It is interesting to compare these results with those for divalent $_{70}$Yb metal,[15] which also has fully occupied $4f$ bands. Unlike the $4f$ bands in $_{71}$Lu, the $4f_{7/2}$ band of $_{70}$Yb is located only 0.3 eV below E_F. This lowering of the f bands in $_{71}$Lu results in a much reduced f character of the wave functions at the Fermi level and, as a consequence, $_{71}$Lu resembles the transition metals $_{21}$Sc and $_{39}$Y. Note, however, that the ground-state LDA eigenvalues of the $4f$ bands in Lu are still too close to the Fermi level compared with the experimental photoemission (PES) values[16] ($\sim$7.0 eV below), as is also the case in $_{29}$Cu for its completely filled $3d$ band. In order to account for Coulomb correlation and relaxation effects and to obtain the correct $4f$ excitation energy, total energy differences between the ground and excited state (with one $4f$ hole) should be carried out.[17]

The total density of states (DOS) of hcp Lu is plotted in Fig. 2 and angular momentum decomposed density of states and charges at the Fermi level are given in Table I. Note that the two sharp peaks in the DOS arising from the $4f$ band are located near the bottom of the conduction band and that the DOS contributions from the d electrons are dominant at E_F. Only 0.02 conduction f electron states are occupied in addition to the fully occupied 14 localized f electrons, which also indicates that the electronic configuration is like that of a typical transition metal.

The temperature-independent behavior of the magnetic susceptibility[18] in Lu can be largely accounted for by the Pauli paramagnetism for a metal with three conduction electrons. Including a calculated Stoner exchange enhancement factor ($S=4.2$), we obtain an exchange enhanced Pauli susceptibility $\chi=2.9\times10^{-4}$ emu/mole. The small difference from the experimental value, $\chi=2.0\times10^{-4}$ emu/mole, seems satisfactory in view of our neglect of the diamagnetism due to conduction and core electrons and of the conduction-electron orbital contributions.

In order to study the cohesive properties, we performed total energy calculations for hcp Lu and, for comparison, fcc Lu as well. In the first set of calculations, the valence electrons, including the f electrons are treated semirelativistically, in which approach all the relativistic contributions except spin-orbit interaction are considered. It is known that neglecting the spin-orbit interaction will not have large effects on the cohesive properties when the $4f$ bands are fully occupied.[19] Minimizing the total energy yields a Wigner-Seitz radius, $r_{WS}=3.55$ a.u., which is

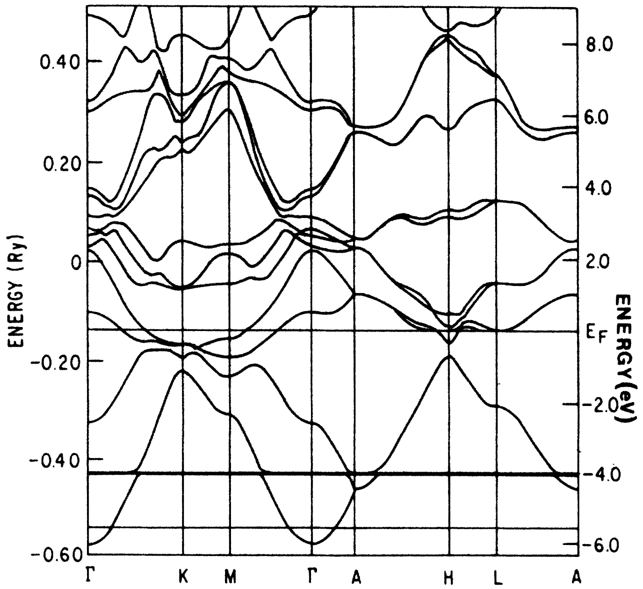

FIG. 1. Relativistic self-consistent electronic band structure of hcp Lu at the experimental lattice constant ($r_{WS}=3.62$ a.u.).

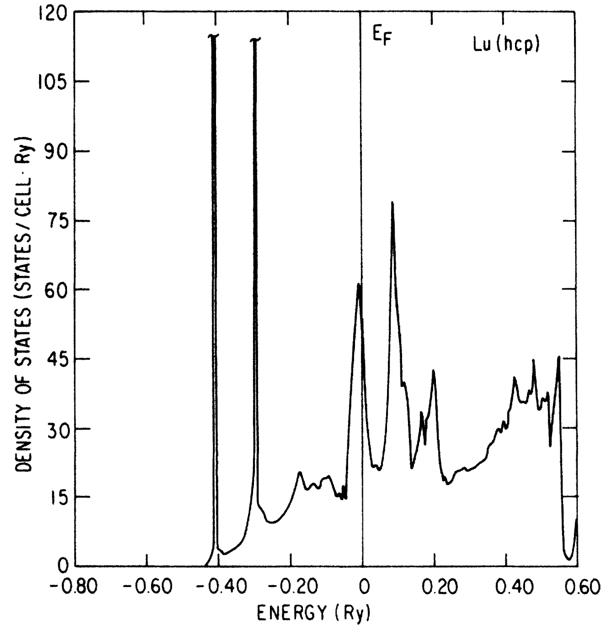

FIG. 2. Total density of states of hcp Lu per unit cell (two atoms) and per Ry.

TABLE I. Angular momentum decomposed density of states at the Fermi level, $N_l\ (E_F)$ (in states/Ry), and charge occupancies Q_l of hcp Lu ($r_{\mathrm{WS}}=3.62$ a.u.).

	s	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$	Total
$N_l(E_F)$	0.23	3.30	5.89	7.74	9.74	0.22	0.47	27.59
Q_l	0.88	0.28	0.42	0.56	0.84	6.01	8.01	17.00

about 2% smaller than the experimental value ($r_{\mathrm{WS}}=3.62$ a.u.). The bonding of the f electrons is usually overestimated in the LDA due to an incomplete description of the strong Coulomb correlation of the f electrons. However, when compared with predictions[15,20] of the LDA for the lattice constants of $4f$ materials with partially filled $4f$ bands (i.e., for $_{58}$Ce, 6%; for $_{63}$Eu, 13% for $_{70}$Yb, 7%), the error for Lu is seen to be much smaller. The completely occupied $4f$ bands in Lu are located far below E_F and the f character near E_F is negligible. Hence, even in the LDA, the spatial extent of the $4f$ orbitals is small and their contribution to the chemical bonding can almost be neglected entirely. The relative error in the description of the $4f$ band in Lu is therefore not important since the absolute value of the bonding energy remains small and, consequently, this relative error only slightly influences the cohesive properties of Lu.

It is also possible to model the localized f-electron nature of Lu by treating the f electrons as core electrons, which means neglecting all band effects of these f electrons. In fact, we obtain almost the same magnitude of the $4f$ spin-orbit splitting (1.54 eV) as in the case of treating the f electrons as valence bands. The calculated equilibrium lattice constant, $r_{\mathrm{WS}}=3.65$ a.u., is now closer to the experimental value (i.e., 1% larger). Note that it is 3% larger than that obtained with our previous treatment of the $4f$ electrons as band states. This indicates that in the LDA, the $4f$ electrons will still have some effect on the cohesive energy, which is not surprising since Lu is experimentally still classified as a rare-earth material.

The calculated equilibrium lattice constants and the corresponding ground-state properties are presented in Table II for both the hcp and fcc structures. The rows indicated with "$4f$ valence" present results with the $4f$ electrons treated in the standard LDA. The rows of "$4f$ core" contain results in which all hybridization and overlap terms are neglected for the $4f$ electrons. The total energy calculations correctly predict the hcp structure as the stable Lu ground state with the total energy of the fcc structure higher by 2—3 mRy. We find that the bulk moduli and cohesive energies are overestimated compared with the experimental values-results that are similar to the situation that commonly occurs in LDA description of transition metals.[21] Note that these quantities are closer to the experimental ones when we neglect the hybridization and overlap of the $4f$ electrons (the $4f$-core case).

III. STRUCTURAL TRANSITIONS UNDER PRESSURE

The structural properties of Lu under pressure were investigated with a self-consistent total energy approach for the hcp, Sm-type, double hcp (dhcp), and fcc structures. These structures are closely related through the sequence in which the hexagonal layers of the atoms are stacked.[22] According to the ways of adding successive layers in the z direction, it can be considered that hcp has 100% hexagonal character, Sm-type has 66.7% hexagonal and 33.3% cubic character, dhcp has 50% hexagonal and 50% cubic character, and fcc has 100% cubic character. Since all these structures are close packed, the LMTO method can be used to calculate the total energy consistently.

Duthie and Pettifor[3] found that structural transitions are not sensitive with respect to the axial values of c/a; hence, we assume the ideal value ($c/a=1.63$) for all the structures. Since we have seen that the $4f$ electrons do not play an important role in the bonding, we treat the $4f$ electrons as core in this study, which makes the calculations effectively fast. In fact, although the $4f_{7/2}$ level moves up toward the Fermi level with increasing pressure, it still lies deep enough in energy to maintain its localized nature (from 3.9 eV below E_F at $r_{\mathrm{WS}}=3.62$ a.u. to 3.1 eV below E_F at $r_{\mathrm{WS}}=3.3$ a.u.). Such a treatment is also justified by the fact that almost the same lattice constant in the structural transition from hcp to fcc is obtained in both ways of treating the $4f$ electrons, i.e., as either

TABLE II. Total energies E_{tot}, equilibrium Wigner-Seitz radii r_{WS}, bulk moduli B, and cohesive energies E_{coh} of hcp and fcc Lu. The $4f$ electrons are treated as either valence band, or as core, by neglecting $4f$ overlap and hybridization.

		E_{tot} (Ry)	r_{WS} (a.u.)	B (Mbar)	E_{coh} (eV)
Experiment	hcp		3.62	0.41	4.43
$4f$ valence	hcp	−29 144.1648	3.55	0.68	5.01
	fcc	−29 144.1626	3.54	0.59	4.98
$4f$ core	hcp	−29 144.1464	3.65	0.63	4.76
	fcc	−29 144.1433	3.64	0.59	4.72

TABLE III. Total energies E_{tot}, equilibrium Wigner-Seitz radii r_{WS}, bulk moduli B, and cohesive energies E_{coh} of hcp, Sm-type, dhcp, and fcc Lu. $4f$ electrons are treated as core in this case.

	E_{tot} (Ry)	r_{WS} (a.u.)	B (Mbar)	E_{coh} (eV)
hcp	−29 144.1464	3.65	0.63	4.76
Sm-type	−29 144.1459	3.65	0.61	4.76
dhcp	−29 144.1454	3.64	0.60	4.75
fcc	−29 144.1433	3.64	0.59	4.72

valence or core electrons ($r_{\mathrm{WS}} = 3.33$ a.u. for $4f$ as valence and $r_{\mathrm{WS}} = 3.32$ for $4f$ as core).

First we consider a number of the ground-state properties of Lu in different close-packed structures; the results are given in Table III. In agreement with experiment, hcp is the most stable structure with the Sm-type being the next most stable one. (However, the energy differences between them are very small but just within the precision of the calculations.) Note, in all cases, that their bulk moduli and cohesive energies are, for all purposes, identical. As an indication of the structural transitions with pressure, we demonstrate in Fig. 3 total energy differences between the structures plotted with respect to the energy of the fcc phase. The first structural transition is from hcp to Sm-type followed by the Sm-dhcp-fcc sequence, which is exactly the same as occurs in the crystal structures when going from right to left in the trivalent rare-earth metal series. Except for our obtaining correctly the ground state as hcp, these results are similar to those obtained by Skriver.[5]

The predicted structural transition from hcp to Sm-type occurs at $r_{\mathrm{WS}} = 3.48$ a.u. ($V/V_0 = 0.89$), which corresponds to the pressure $P \sim 110$ kbar. Compared with the transition pressure ($P \sim 230$ kbar) observed by Liu,[1] our theoretical value is smaller by a factor of 2. The second structural transition from Sm-type to dhcp is predicted to occur at $r_{\mathrm{WS}} = 3.3$ a.u. ($V/V_0 = 0.76$, $P = 325$ kbar), and the third one from dhcp to fcc at $r_{\mathrm{WS}} = 3.05$ a.u. ($V/V_0 = 0.60$, $P = 925$ kbar). It should be noted that we consider only the static structural properties in this study. Phonon effects, which might play an important role in determining the stable crystal structure, have not been included. The discrepancy in transition pressure between experiment and calculation may originate from these finite-temperature effects. The experiment was performed at room temperature, whereas our calculations are for $T = 0$ K. Since the structural energy differences are much less than 1 mRy (150 K), the temperature will be an important factor. Hence, comparisons of our results with experimental results at low temperatures will be more suitable.

It is of some interest that *sp*- to *d*-electron transfer occurs with applied pressure, since the *d* band moves down in energy with respect to the *sp* band. Generally speaking, the *sp* electrons are more sensitive to pressure because of their large spatial extent. With applied pressure, the increase of the kinetic energy of the *sp* electrons is much larger than that of the *d* electrons; hence, the *sp* band moves up with respect to the *d* band. This change of *d* occupancy is believed to determine the stable structure under pressure.[3,23] Figure 4 plots the occupation number of *s*, *p*, and *d* electrons of Lu as a function of the Wigner-Seitz radius and also shows the stable structures. One sees that the stable structures for the range of *d* occupancy are hcp for $N_d < 1.52$, Sm-type for $1.52 < N_d < 1.65$, dhcp for $1.65 < N_d < 1.8$, and fcc for $N_d > 1.8$. This correlation between the stable structures and *d*-occupation number can be related to the crystal-structure sequence as observed in the trivalent rare-earth-metal series, as discussed in Sec. IV.

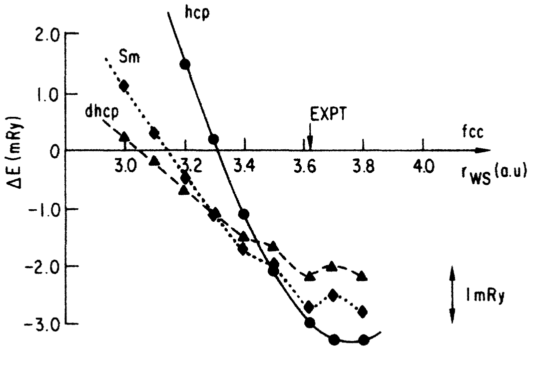

FIG. 3. Structural transitions with pressure between the four close-packed structures: hcp, Sm-type, dhcp, and fcc. Total energy difference with respect to that of fcc are drawn as a function of Wigner-Seitz radius.

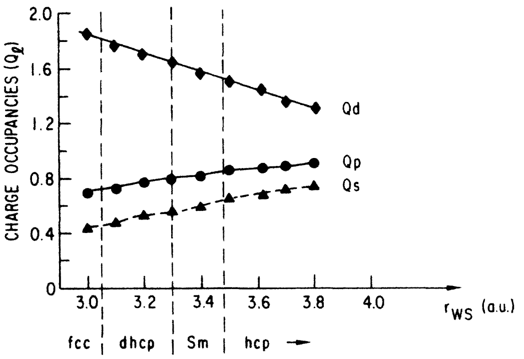

FIG. 4. Change of occupancies (*s*, *p*, and *d* character) with pressure. The corresponding ranges for the stable structures are indicated. $4f$ electrons are treated as core in this case.

IV. DISCUSSION OF THE RELATION TO STRUCTURAL PHASES OF THE RARE-EARTH METALS

In Sec. III we have seen that the structural behavior of Lu under pressure reproduces the sequence of the crystal structures which is observed in the trivalent rare-earth metals. The increase of *d* occupancy when going from right to left across the rare-earth series can be considered to be similar to the increase of *d* occupancy in Lu with pressure. When we consider the structural properties of Lu, we neglect *f*-bonding effects by treating them as part of the core. As a result, the structural sequence obtained for Lu can be considered to come dominantly from the bonding of the *d* electrons. This may be considered to give additional convincing evidence that the 4*f* electrons do not play an important role in determining the stable crystal structures in the heavy rare-earth metals.

A one-to-one correspondence of the *d*-band occupancy between the real rare-earth metals and Lu under pressure is not perfect; self-consistent band-structure calculations[17] show that there is about a 0.2 difference between the number of *d* electrons in the rare-earth metals and that predicted for Lu under pressure. In the trivalent rare-earth materials, the hcp structure is stable for the range of *d* occupancy $N_d < 1.7$ compared with the case of Lu for $N_d < 1.52$; Sm metal has about 1.77 *d* electrons compared with the prediction of a stable Sm-type structure in Lu for $1.52 < N_d < 1.65$; and the dhcp structure is stable in the rare-earth metals for $1.83 < N_d < 1.98$, whereas $1.65 < N_d < 1.8$ in Lu. These results indicate that a simple rigid band concept does not work for a quantitative description of the structural properties in the trivalent rare-earth series, even though it gives the correct structural sequence. Clearly, the different nature of 4*f*-electron localization and core electron screening should be taken into account properly in each material.

One always faces difficulties in describing the localized nature of the *f* electrons. Since Lu behaves like a *d*-band rather than an *f*-band metal, it can be properly described within the LDA by treating the *f* electrons as part of the core. We found[17] that such an LDA approach can be used for the heavy rare-earth metals to predict the equilibrium lattice constants in close agreement with the experimental values. In the case of the light rare-earth metals (for example, $_{58}$Ce, $_{59}$Pr, $_{60}$Nd, $_{61}$Pm), however, additional bonding effects from the *f* electrons need to be properly included in order to obtain the correct experimental lattice constants. By contrast, the application of the LDA which treats *f* electrons as valence bands overestimates the *f*-electron bonding effects and gives much smaller lattice constants.

In summary, we have investigated the ground-state electronic structure of Lu metal using self-consistent total energy LMTO band-structure calculations. We have obtained the result that Lu behaves like a *d*-band transition metal. We have also studied the structural properties under pressure and compared them with experiment. The sequence of crystal structures observed in the trivalent rare-earth materials is reproduced in the pressure induced structural transitions in Lu, which gives an interesting evidence for the correlation between the amount of *d* occupation and the stable crystal structure.

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