Calculated high-pressure-induced electronic and structural phase transitions in Sr and Yb up to 50 kbar

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The energy band structures of Sr and Yb have been calculated by the linear-muffin-tin-orbital–atomic sphere approximation method in the pressure range of 0–50 kbar. By the inclusion of nonlocal exchange corrections to the local-density approximation, excellent agreement with regard to experiment has been found in predicting the electronic and structural phase transition pressures of these elements. [S0163-1829(96)05648-2]

It has been a challenge in condensed-matter physics to investigate the effect of pressure on the electronic and structural properties of divalent metals from the time of Bridgman's first paper almost 70 years ago.[1] The band-structure calculations, based on the local-density approximation (LDA) of the density-functional theory,[2] qualitatively explained[3–8] the essential mechanisms of these effects for Sr and Yb in terms of the sp-d hybridization and the charge transfer. However, adverse results with regard to experiment have been reported quantitatively, even for the simple Ca metal.[9] Experimentally,[10–14] Sr and Yb at ordinary pressures are normal metals. Under pressure fcc Sr becomes a semimetal, remains in that state up to 35 kbar, and in the bcc phase above 35-kbar Sr is metallic. Under pressure fcc Yb also becomes a semimetal. It is semimetallic up to 14 kbar and semiconducting between 14 and 40 kbar. In the bcc phase above 40-kbar Yb is metallic. Theoretically, Sr is found to be semimetallic[5,15] and Yb semiconducting[3,5] at normal pressures. According to Skriver,[5] Sr becomes a semiconductor at 3-kbar and fcc→bcc transition occurs at 40 kbar. Kubo[7] has found that Yb remains in the state of a semimetal under high pressure. The critical pressure for the fcc→bcc transition in Yb is found to be 49, 50, and 5 kbar in Refs. 4, 5, and 8, respectively.

The importance of the nonlocal nature of the exchange-correlation potential was first pointed out by Vasvari, Animalu, and Heine.[16] Later, Jan and Skriver[9] emphasized that in order to obtain a quantitative description, nonlocal effects should be included. Very recently, substantial improvement has been reported on the band-structure calculations of heavy alkali metals[17] and alkaline-earth metals,[18] by use of the Langreth-Perdew-Mehl[19] (LPM) exchange-correlation potential (ECP) which favors inhomogeneous electron gas and includes nonlocal exchange corrections to the LDA. Except for the $4f$ electrons, Yb and Sr are similar systems and therefore it is reasonable to expect a quantitative improvement for Yb within the LPM scheme, which constitutes the main objective of the present work.

For this purpose, electronic band-structure calculations for Sr and Yb are carried out self-consistently by means of

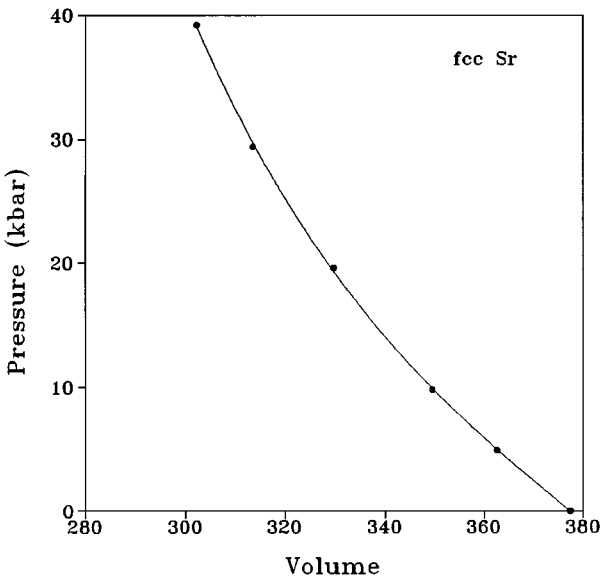

FIG. 1. Pressure as a function of atomic volume (in a.u.) for fcc Sr. The solid line refers to a cubic polynomial fit of the experimental data (Ref. 23).

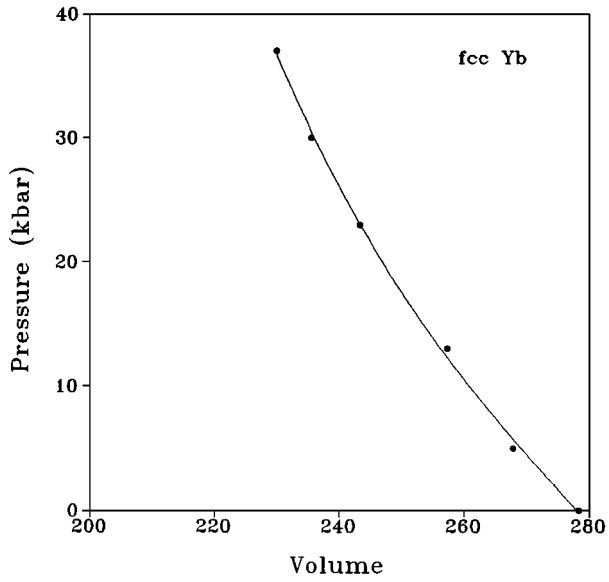

FIG. 2. Pressure as a function of atomic volume for fcc Yb. The solid line refers to a cubic polynomial fit of the experimental data (Ref. 14).

TABLE I. Calculated specific-heat coefficients (in mJ mol^{-1} K^{-2}) for fcc Sr and Yb.

	Sr	Yb
Johansen and Mackintosh[a]		0.00
Skriver[b]		0.00
Sankar, Iyakutti, and Dakshinamoorthy[c]		1.83
Kubo[d]	2.57	2.08
Sigalas and Papaconstantopoulos[e]	0.00	
BH (present work)	1.15	0.27
LPM (present work)	3.43	1.56
Experiment	3.64[f]	2.90[g]

[a]Reference 3.
[b]Reference 5.
[c]Reference 6.
[d]Reference 7.
[e]Reference 15.
[f]Reference 24
[g]Reference 25.

TABLE II. Variation of the total density of states at the Fermi level, $N(E_F)$ (states/Ry atom), as a function of pressure (in kbar) for fcc Sr within the LPM formalism.

Pressure	$N(E_F)$
0.0	19.79
4.9	6.38
9.9	0.36
19.3	0.10
29.7	0.03
34.0	0.01

TABLE III. Effect of pressure (in kbar) on the total-energy difference ΔE (in Ry) of Sr in the fcc and bcc structures.

Pressure	$\Delta E \times 10^6$
29.7	−104
32.2	−45
34.0	7
35.8	51
37.3	79
39.1	124

TABLE IV. Effect of pressure (in kbar) on the total-energy difference ΔE (in Ry) of Yb in the fcc and bcc structures.

Pressure	$\Delta E \times 10^6$
32.6	−165
34.7	−84
36.7	−50
38.9	−4
41.2	59
43.5	124
45.9	218

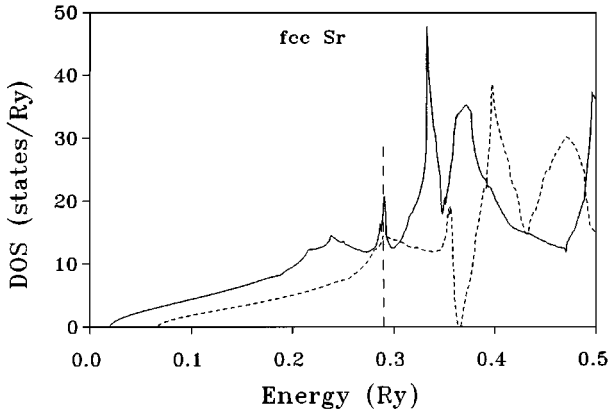

FIG. 3. The total density-of-states (DOS) curves for fcc Sr obtained within the LPM scheme at normal pressure (solid curve) and at 34 kbar (dashed curve). The vertical dashed line indicates the position of the Fermi level for the solid curve at 0.290 Ry. For the dashed curve, Fermi level is at the dip positioned at 0.366 Ry.

the linear-muffin-tin-orbital (LMTO) method[20] within the atomic sphere approximation (ASA), using the codes of Skriver.[21] The combined correction terms to the ASA are included for the fcc and bcc structures considered. All the calculations were performed within the LPM and von Barth-Hedin[22] (BH) exchange-correlation formalisms. As pointed out by Kubo,[7] it needs a very accurate calculation of the density of states (DOS) in order to investigate the effect of pressure quantitatively. Preliminary calculations for DOS values, which were obtained by the tetrahedron method, also confirmed this and for Sr, we have used 1876 and 1785 k points in the irreducible wedge of the Brillouin zone for fcc and bcc structures, respectively. For Yb, the number of k points used were 1505 and 1496 for fcc and bcc structures, respectively. The total DOS at the Fermi level, $N(E_F)$, is calculated as described in Ref. 18. The self-consistency is achieved in such a way that total-energy values, calculated within the frozen core approximation, between the consecutive iterations was better than ± 0.005 mRy. Although it is not very definite, d electrons of Sr and f electrons of Yb are

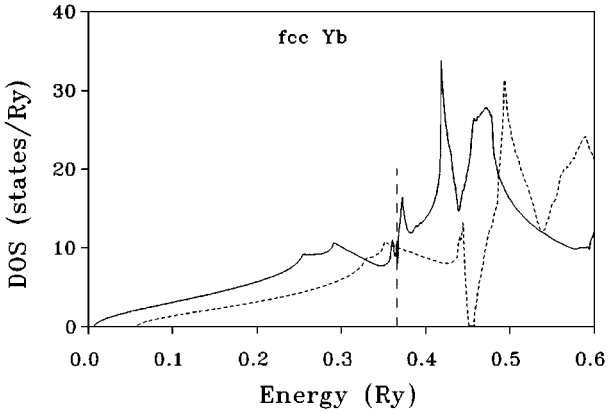

FIG. 4. The total density-of-states (DOS) curves for fcc Yb obtained within the LPM scheme at normal pressure (solid curve) and at 39 kbar (dashed curve). The vertical dashed line indicates the position of the Fermi level for the solid curve at 0.366 Ry. For the dashed curve, Fermi level is at the dip positioned at 0.453 Ry.

TABLE V. Summary of the calculated electronic and structural properties for Sr and Yb under high pressure.

Exchange-correlation potential	Metal→semiconductor transition pressure (kbar)		Semiconducting gap (meV)		fcc→bcc transition pressure (kbar)	
	Sr	Yb	Sr	Yb	Sr	Yb
BH	19.0	5.6	27	14	21	29
LPM	semimetal	11.8	0	54	34	39
Experiment[a]	semimetal	14.0	0	80	35	40

[a]References 10–14.

treated as core electrons and in order to make reliable comparisons with the experiment, all the calculations were performed at the experimental pressures. For fcc Sr we have used the Bridgman's values,[23] whereas compression data[14] up to 37 kbar was used for fcc Yb. The pressure as a function of atomic volume are shown for Sr and Yb in Figs. 1 and 2, respectively.

Specific-heat coefficients γ (in mJ mol^{-1}K^{-2}) calculated at normal pressure for Sr (Wigner-Seitz radius $S=4.483$ a.u.) and Yb ($S=4.051$ a.u.) are presented in Table I. Results of the previous work and experimental data are also given for comparison. According to Table I, use of the LPM potential yields consistent results when compared with the local BH or other LDA based ECP's for Sr. The discrepancy with the Kubo's result can be attributed to the use of a different ECP, S value, and k-point sampling. For Yb, we should note that γ value is very sensitive to the choice of the S value due to the hyperfine structure of the DOS curve in the vicinity of the Fermi level. If the S value is taken, as in Ref. 26, to be 4.063 a.u., the corresponding γ value becomes 2.14 within the LPM scheme. On the other hand, the experimental γ value for fcc Yb is rather confusing. According to Bucher *et al.*,[27] Lounasmaa's data[25] apply to the hcp phase and for fcc Yb, γ value is equal to 8.36 mJ K^{-2}. In any case it is evident that, as admitted by Kubo,[7] LDA potentials do not work well for Yb. We therefore suggest that fully relativistic calculations within the LPM scheme should be considered and in that context, more sensitive measurements should be performed for fcc Yb under normal pressure.

In Table II, calculated $N(E_F)$ values as a function of pressure are presented for fcc Sr. It is clearly seen that Sr becomes a semimetal under high pressure and remains in that state up to 34 kbar. This is also confirmed by Fig. 3 in which the total DOS curves are shown at normal pressure and at 34 kbar. In order to determine the fcc→bcc transition pressure, extensive calculations have been performed in the pressure range of 30–39 kbar and the results are given in Table III. At 34 kbar, the total energy difference ΔE for fcc and bcc Sr is almost zero within the self-consistency criterion. At about 36 kbar, ΔE is equal to 0.051 mRy and safely distinguishable. We should note that the results obtained for Sr within the LPM formalism are in excellent agreement with the experimental observations. On the other hand, the BH scheme yields incorrect results in that Sr becomes a semiconductor at 19 kbar and structural phase transition occurs at about 21 kbar.

In Fig. 4, the total DOS curves for fcc Yb are shown at normal pressure and at about 39 kbar. Within the LPM scheme, we have found that Yb becomes a semiconductor at about 12 kbar, remains in that state up to 39 kbar, and transforms to the bcc structure at about 40 kbar (Table IV) in excellent agreement with the experimental data. Again the BH formalism yields incorrect results with regard to experiment as presented in Table V.

In summary, we have performed LMTO-ASA calculations of Sr and Yb in the pressure range of 0–50 kbar. It is found that inclusion of nonlocal corrections to the local-density approximation (LDA) yields substantial improvement in predicting the effect of pressure on the electronic and structural phase transitions of Sr and Yb. It is emphasized that errors occur in the LDA based theoretical calculations for the systems which have small valence-charge densities and it is concluded that these systems should be treated within the LPM scheme. However, it should not be the intent to generalize this for all materials and for all ECP's used in the electronic structure calculation methods, since not only the method but also the choice of the ECP suitable for that method should be considered to obtain reliable results.

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