PHYSICAL REVIEW B VOLUME 52, NUMBER 12 15 SEPTEMBER 1995-II

Density-functional approach to the valence change in SmS: Normal and high-pressure phases

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(Received 4 May 1995)

The electronic structure of SmS in dependence of the lattice constant is calculated by means of density-functional theory. The local-density approximation (LDA) to the exchange and correlation potential is employed. The $4f$ electrons, however, are treated in three different ways, viz., (i) as localized core states, (ii) as extended band states, and (iii) as self-interaction corrected (SIC) band states. While the experimentally observed Sm valency of normal state SmS (black phase) cannot be described by methods (i) and (ii) the SIC calculations are consistent with the measured value. For pressures above 30 kbar, method (ii) agrees well with the observed Sm valency, whereas methods (i) and (iii) fail. Therefore we conclude that the phase transition in SmS is very similiar to the α-γ transition in Ce metal. The SIC band structure shows the splitting between the occupied and empty $4f$ states due to the large on-site electron correlation. The Fermi level ϵ_F is situated in the gap between the S $3p$ states and the Sm band states mainly of $5d$ character. In the high-pressure phase the $4f$ states presumably become delocalized, resulting in vanishing self-interaction corrections. Therefore the uncorrected LDA results are appropriate for the high-pressure phase.

I. INTRODUCTION

The electronic structure of SmS has attracted much attention during the last years.[1-7] This permanent interest is mainly due to the fact that the material shows an isostructural first-order phase transition at a pressure of 6.5 kbar, which is accompanied by dramatic changes in the electronic system, manifesting itself in a spectacular color change from black to golden,[8,9] and also in the lattice dynamics. For SmS under normal conditions (i.e., in the black phase), there is no doubt that the material is semiconducting and the samarium ions have valency 2^+, at least with only very small deviation, being in the $^7F_0$ ionic ground state. For the golden phase, the situation is not as clear. It seems to be necessary to consider two different regions. The first region, directly above the phase transition, is mixed valent, with a samarium valency of about 2.6 from spectroscopic methods and susceptibility measurements[10-13] and about 2.8 from the Vegards-law analysis of lattice constant measurements.[13] A puzzling fact is the temperature dependence of the resistivity, which is semiconductorlike.[14,15] Also, the point-contact experiments[9] and the far-infrared spectroscopy[16] show that there is a gap of 7 meV. Although this gap is wider than the gap measured in the related compound SmB_6, the conductivity at 4 K is larger by several orders of magnitude. The latter fact in connection with the argument that the parity of the lowest d band between Γ and X in SmS is different from that of SmB_6 suggests that there is only a pseudogap present.[17,18] At pressures above 30 kbar, the temperature dependence of the resistivity turns to a more or less metallic behavior at low temperatures[15] and the valency increases towards 3. From measurements of the transport properties,[14] it was concluded that it is very close to 3; whereas from L_{III} absorption, a value of 2.9 was derived for 72 kbar.[10] Although most of the experimental work was carried out 20 years ago, high-quality band structure calculations have been done only in the last decade. The first fully relativistic and self-consistent band structure was given by Strange,[3] using the linear muffin-tin orbital method. In his calculation, spin-orbit coupling yields a splitting of about 0.6 eV between the $4f_{5/2}$ states and the $4f_{7/2}$ states. At normal volume, these two bands are crossed by the lowest $5d$ band resulting in a metallic behavior. For a volume exceeding the experimental volume by 5%, a gap of about 130 meV is found between the $4f_{5/2}$ states and the $5d$ band. By decreasing the lattice constant, the d bands broaden till the lowest d band lies completely below the f bands. This happens at 80% of the normal volume. Although these calculations provide an intriguing picture of the valence transition and also of the semiconductor to metal transition, they cannot account for the splitting of filled and empty f bands, which is expected to be 6–7 eV from x-ray photoemission spectroscopy[19] and bremsstrahlung isochromat spectroscopy[20] measurements. Lopez-Aguilar and Costa-Quintana[4] tried to overcome this drawback by introducing the Coulomb correlation "by hand," thus extending the Kohn-Sham equations by an additional Hubbard-U term, which distinguishes between the occupied and unoccupied states. Consequently, they found a semiconducting state due to the Hubbard-like splitting between the occupied and unoccupied bands. Since the underlying uncorrelated band structure was calculated without taking into account relativistic effects, the results may have qualitative significance, but the spin-orbit splitting is not reflected. Lu *et al.*[6] studied the applicability of the local-density approximation (LDA) in a systematic way. The full potential linearized augmented plane wave (FLAPW) calculations used include spin-orbit coupling and nonspherical potential terms and therefore provide accurate *ab initio* results. If these authors treat the $4f$ states as band states, they find no dramatic change in the band structure by variation of the volume between 0.6 and 1.4 times the experimental value. The FLAPW band structures disagree with the results given by Strange,[3] but are in accordance with our findings as will be shown below. From a total energy calculation, Lu *et al.* determined the equilibrium lattice constant to be 5.52 Å. On the other hand, they calculated the value 5.89 Å, if they put the $4f$ electrons into the core. The related experimental lattice constants are 5.67 Å in the mixed valence (MV) state and 5.97 Å in the normal state, respectively. Furthermore, this calculation showed that the bulk modulus fits much better to the experimental value of the normal phase, if the $4f$ states are treated as core states. Drawing the conclusion that the LDA provides an inadequate description of the $4f$ electrons in SmS, the authors refer to the Ce (Ref. 21) problem, where the situation was the same. It was this analogy that motivated us to reconsider the band structure of SmS in light of the results on cerium,[22,23] which are a breakthrough in the density-functional treatment of the γ-α transition. The inclusion of the self-interaction correction (SIC) to the localized electron states provides a tool to handle occupied and unoccupied states differently in an *ab initio* calculation. The aim of the present paper is to investigate three different approximations to density-functional theory with respect to their ability to describe the Sm $4f$ occupation and related properties of SmS. The mean $4f$ occupation number determines the electron density $n(\mathbf{r})$ and is, consequently, a ground state property. In Sec. II, results are presented for LDA calculations with $4f$ orbitals treated as core states. Section III is devoted to conventional LDA calculations. The effect of self-interaction corrections to the electronic structure is discussed in Sec. IV.

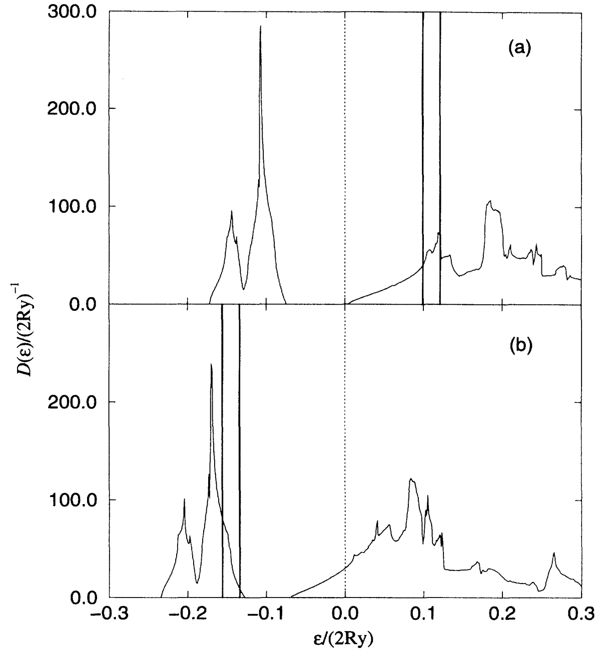

FIG. 1. The density of states for SmS with $4f$ states treated as core states. The lattice constant is 5.97 Å. (a) $4f$ occupation fixed to six, (b) $4f$ occupation fixed to five. The thick lines mark the position of the $4f$ core levels. The inconsistency of case (a) lies in the fact that the $4f_{5/2}$ levels (assumed to be occupied) are above the Fermi level. Case (b) on the contrary yields inconsistently the $4f_{7/2}$ levels (assumed to be empty) below the Fermi level (ϵ_F=0).

II. 4*f* ELECTRONS TREATED AS CORE ELECTRONS

Motivated by the finding of Lu *et al.*[6] that the LDA with $4f$ orbitals included in the band provides an inadequate description of normal-state SmS (with experimental lattice constant 5.97 Å), we calculated the band structure with the occupation of the $4f$ core states fixed to five and six, respectively. Since the core f states were not allowed to hybridize with band states, their final energy levels are determined to first order in the crystal field (the difference between the LDA crystal potential and a spherical atomic site potential). It is obvious that the resulting picture (Fig. 1) displays in both cases an unstable electron configuration. If the configuration is $4f^6$, the Fermi energy is far below the occupied $4f_{5/2}$ levels. On the other hand, if the $4f$ configuration is $4f^5$, the Fermi level is much higher than the position of the unoccupied $4f$ levels. This argumentation rests on the assumption that the Kohn-Sham occupation rule, valid in a rigorous density-functional theory, could be applied as well to the case of localized $4f$ states (in combination with the LDA), which are simulated as a partially occupied core shell:

$$n(\mathbf{r}) = \sum_{\mathbf{k}} |\Psi_{\mathbf{k}}(\mathbf{r})|^2 \Theta(\epsilon_F - \epsilon_{\mathbf{k}}) + \sum_{4f} |\Psi_{4f}(\mathbf{r})|^2 \Theta(\epsilon_F - \epsilon_{4f}),$$

$$N = \sum_{\mathbf{k}} \Theta(\epsilon_F - \epsilon_{\mathbf{k}}) + \sum_{4f} \Theta(\epsilon_F - \epsilon_{4f}),$$

where $n(\mathbf{r})$ is the electron density, $\Psi_{\mathbf{k}}$ and Ψ_{4f} are one-particle wave functions of band and $4f$ states, respectively, with related eigenvalues $\epsilon_{\mathbf{k}}$ and ϵ_{4f}, N is the electron number, ϵ_F is the Fermi level determined by the second equation, and Θ is the step function. In order to find the occupation number, where the $4f$ levels are at the Fermi energy, we varied the occupation number between five and six. These calculations resemble the work of Dederichs *et al.*,[24] who fixed noninteger occupation numbers with the help of Lagrange multipliers.

The results shown in Fig. 2 correspond to the lattice

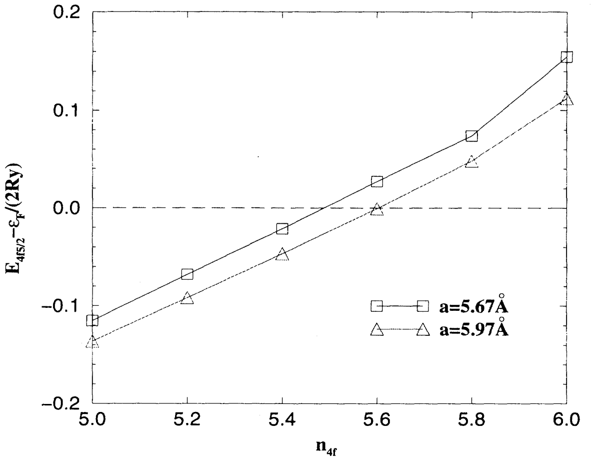

FIG. 2. The position of the $4f_{5/2}$ levels relative to the Fermi level in dependence on the occupation number of the $4f$ core states. The $4f$ occupation number was fixed by hand during the calculation. The parameters at the curve are the lattice constants. The lines are guides to the eyes.

constant in the normal state (a =5.97 Å) and in the MV state (a=5.67 Å), respectively. Accepting the state where the sixfold degenerate $4f_{5/2}$ level is at the Fermi energy as a stable electron configuration, one finds the $4f$ occupation to exhibit a very small change from 5.60 to 5.48 only; thus, there is no chance to describe the observed valence change of 0.6–0.8 by means of this method.

III. 4*f* ELECTRONS TREATED AS BAND STATES

In this section we will investigate how the valence depends on the lattice parameter if the $4f$ states are treated as extended states. Two recent calculations due to Lu *et al.*[6] (using a "full potential" LAPW scheme) and later on Masjukova and Farberovich[7] (using a "muffin tin" LAPW scheme) yielded very different results regarding the arrangement of the $4f$ subbands and the total density of states in their dependence on the lattice constant. The probable reason for these differences lies in the better treatment of the potential by Lu *et al.* We employed the optimized linear combination of atomic orbitals method[25] in its full relativistic version.[26] The k sums were done using 1511 k points in the irreducible part of the Brillouin zone. The results of our calculation agree very well with the results given in Ref. 6. In Fig. 3 the total overall band structure and the total density of states is shown. The band structure for different lattice constants is plotted in Fig. 4. Starting from a hypothetical system with an expanded lattice with a=6.17 Å, we inspected the change with decreasing lattice parameter going to a =5.57 Å, corresponding to very high pressure. We confirm the statement given in Ref. 6 and contradicting both Refs. 3 and 7 that no drastic change occurs in the band structure, neither a gap opens as stated in Ref. 3 nor a rearrangement of the $4f$ peaks occurs like in Ref. 7. For comparison with Refs. 6 and 7, we show in Fig. 5 the total density of states (DOS) in the vicinity of the Fermi energy for both the normal and the compressed phase. The $4f$ net occupation in a Mullikan population analysis shows again small changes only with a variation of the lattice constant (5.49 for a =5.97 Å to 5.36 for a=5.67 Å). The total energy calculations reported in Ref. 6 yielded a lattice constant of 5.52 Å being about 2% less than the value a=5.62 Å interpolated from the adjacent trivalent rare earth sulphides for the hypothetical $Sm^{3+}S$ lattice[27] and 2.5% less than the reported high-pressure lattice constant.[28] This difference is the typical value found by using the LDA. From these results, together with our calculated valency of about 2.68 corresponding to a net $4f$ occupation of 5.32 (a=5.57 Å), it seems to be justified to assume that the conventional LDA description works correctly for the high-pressure phase of SmS, but not for the normal pressure phase.

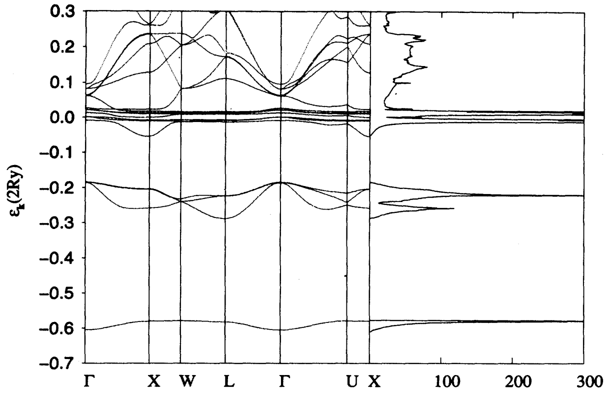

FIG. 3. $4f$ states treated as valence states. The band structure and total density of states for a =5.57 Å (ϵ_F=0). The density of states (at the right-hand side) is given in arbitrary units.

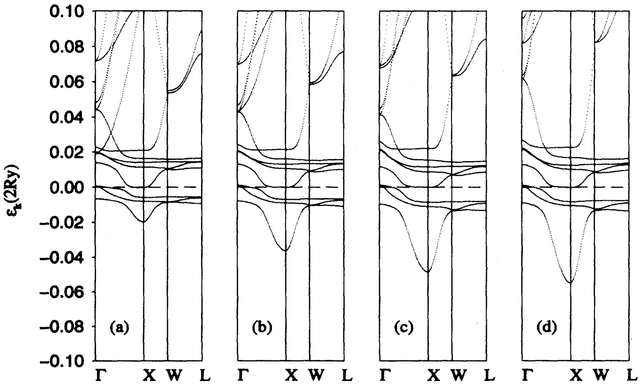

FIG. 4. $4f$ states treated as valence states. The band structure in the vicinity of the Fermi energy (ϵ_F=0) for the lattice constants (a) 6.17 Å, (b) 5.97 Å, (c) 5.77 Å, and (d) 5.57 Å.

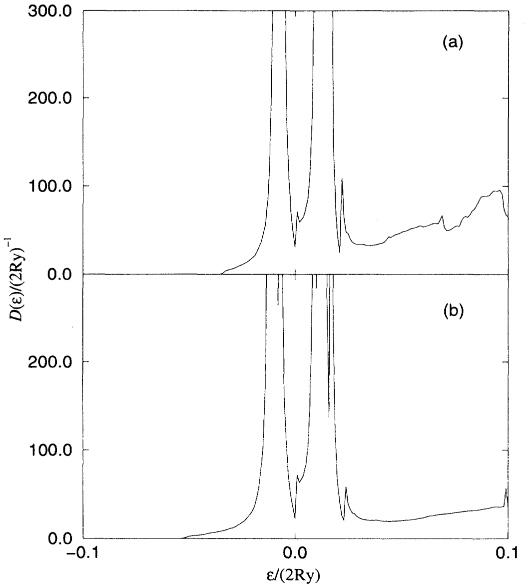

FIG. 5. $4f$ states treated as valence states. The total density of states in the vicinity of the Fermi energy (ϵ_F=0) for (a) 5.97 Å and (b) 5.57 Å.

The partial DOS depicted in Fig. 6 supports the hybridization model as summarized in Ref. 29. This model takes into account a broad d band crossing a narrow $4f$ band and the hybridization between the two bands. Martin and Allen[17] argued within this model that on the grounds of the Luttinger theorem, the Fermi level should be in the midst of a hybridization gap if the $4f$ count is even and in one of the adjacent peaks if the $4f$ count is odd. Clearly the presumptions of the model are too rigid in comparison with the complicated composed structure of the states at the Fermi level. Nevertheless, the calculated DOS at the Fermi level is very small. The reason that it is not zero is the dispersion of the $4f$ band, which was neglected in Ref. 17. From our calculated band structure, it is obvious that there exists a pseudogap and a Fermi surface making the material at least semimetallic (cf. Fig. 4). It should be noted, however, that the resolution of gaps or pseudogaps of some 10 meV is beyond the capabilities of today's band structure schemes and the results on this energy scale depend on details of the potential construction, the wave function basis, etc.

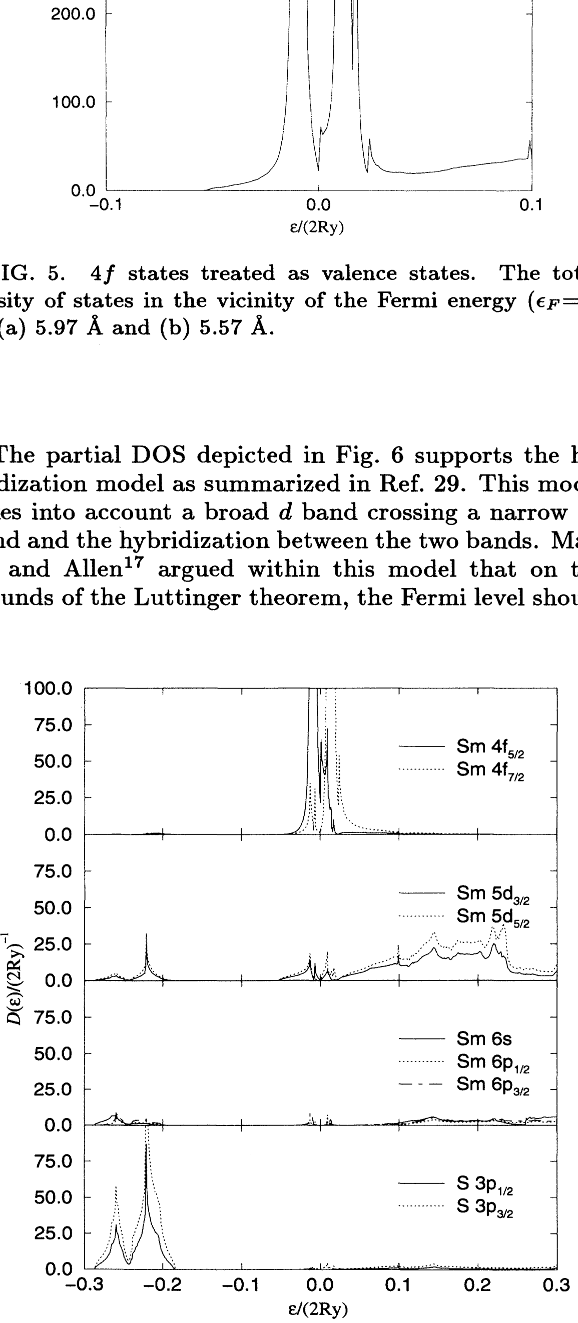

FIG. 6. $4f$ states treated as valence states. The partial densities of states for a =5.57 Å.

IV. SIC-LDA CALCULATIONS

In the preceding sections it was shown that neither the conventional LDA calculation nor the calculation with $4f$ core treatment in LDA can account for the experimentally observed valency of Sm in the ambient pressure phase of SmS. This is similar to the situation in the γ phase of elementary Ce, where the correct lattice parameter is obtained from LDA with $4f^1$ core calculations[21] at the price of violating the Kohn-Sham orbitals occupation rule (we find for Ce $\varepsilon_{4f} \approx \varepsilon_F + 1.5$ eV). Recently, Szotek *et al.*[22] and Svane[23] repaired this blot by introducing SIC to the localized $4f$ states. Together with an uncorrected LDA (Refs. 22 and 23) or a generalized gradient approximation calculation[30] for the low-volume α phase, this method provides the best available first-principles description of the equation of state of Ce.

Self-interaction corrections[31] to the local-density approximation aim at removing the unphysical interaction of a localized electron with the (Hartree and exchange-correlation) potential generated by itself. This self-interaction is not completely canceled in the LDA and thus the corrections improve the LDA for systems with localized states. In particular, the SIC-LDA description is exact for one-electron systems, where the conventional LDA is weak by construction. In the case of atoms, all occupied states are localized and there is no doubt how to apply the self-interaction correction. Related calculations on ionization potentials and electron affinities provide results much closer to experimental data than LDA and Hartree-Fock results.[31]

Including the self-interaction correction to the LDA, calculations on extended systems meet the nontrivial problem of a proper determination of the localized occupied states to be corrected. From a formal point of view, both the number and shape of the localized states had to be varied to minimize the total energy.[31] The present calculation aims at a verification of the compatibility of a SIC-LDA calculation with the experimentally observed valency. Thus, the complete $4f_{5/2}$ subshell containing six states was chosen to be occupied and self-interaction corrected. The radial shape of these states was determined self-consistently, i.e., they are recalculated in each iteration step. The SIC potential was taken in a

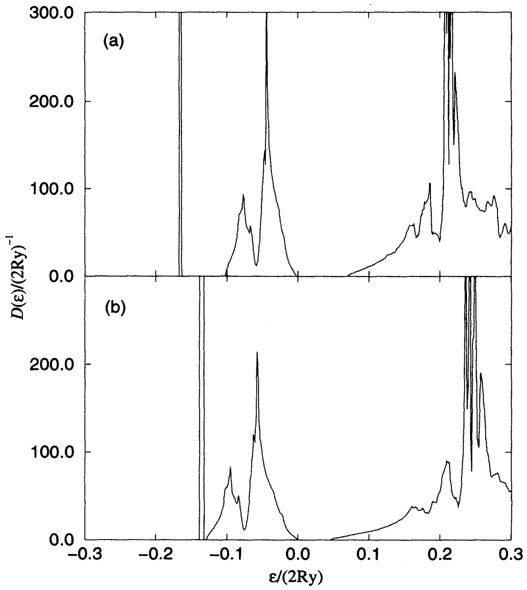

FIG. 7. $4f$ states treated as valence states. The six $4f_{5/2}$ states are self-interaction corrected. The total density of states for (a) $a=5.97$ Å and (b) a=5.57 Å, with ϵ_F=0.

spherical approximation.[32] In atomic systems, orthogonalization corrections for states calculated with slightly state-dependent effective SIC-LDA Hamiltonians are, in general, small.[31] These corrections are neglected in the present calculations.

In Fig. 7, the DOS obtained from SIC-LDA calculations as described above is presented for two different values of the lattice parameter (normal state and strongly compressed). The splitting between the occupied $4f_{5/2}$ and the unoccupied $4f_{7/2}$ states amounts to about 10 eV. This value is larger than the on-site Coulomb correlation energy $U \approx 6$ eV, in accordance with the results by Temmerman *et al.* on elementary Pr.[33] Consequently, the self-interaction corrected occupied $4f$ levels do not fit, as in the aforementioned case of Pr, to the spectroscopic observation of $4f$ states just below ε_F. On the other hand, the main $4f$ peak in the unoccupied part of the DOS is situated about 7 eV above the sulfur $3p$ peak in fair agreement with combined photoelectron and bremsstrahlung isochromate data.[20]

We hesitate to overemphasize the spectroscopic interpretation of the Kohn-Sham (with and without SIC) density of states, having no connection to observable quantities from the formal point of view. The valency is much better suited for comparison with experimental data in Kohn-Sham-like density-functional theories, however, since it is an integral over a projected charge density. It is evident from Fig. 7 that for both lattice parameters considered, the assumed localized configuration $4f^6$ fulfills the Kohn-Sham occupation rule: The $4f$ states assumed to be occupied (SIC applied) and unoccupied (no SIC applied) appear to be well (3 eV–5 eV) below the highest occupied S $3p$ and above the lowest free electron state, respectively. Moreover, no other integer occupation (in particular five) would fulfill this rule, since the Coulomb shift connected with the change of n_{4f} by one (cf. Fig. 2) is larger than 6 eV.

From these considerations it follows that from all calculation schemes applied, only the SIC-LDA method can provide results consistent with the experimentally observed valency of normal-state SmS. In the high-pressure phase, the assumption of all $4f$ states being delocalized (conventional LDA) yields a Sm valency in accordance with the experiment. SIC automatically disappear for completely delocalized states; thus, SIC-LDA is formally equivalent to the conventional LDA in this case. As a final consequence, our calculations support the idea of a $4f$ localized $\longrightarrow$ $4f$ delocalized transition between the normal and high-pressure phases of SmS, as has been suggested for the isostructural $\alpha \longrightarrow \gamma$ phase transition in elementary Ce. In SmS, this transition is accompanied by a valence change in contrast to the isovalent behavior of Ce metal.[34,35]

V. SUMMARY

The valency of SmS has been calculated for different lattice parameters, using the conventional LDA, LDA with $4f$ core treatment, and SIC-LDA. Only the SIC-LDA results, together with the assumption of six localized $4f$ states of Sm, are consistent with the experimentally observed divalent state of Sm in the normal pressure phase of SmS. In the high-pressure phase, conventional LDA calculations yield the correct valency. These findings are consistent with a transition from localized to delocalized $4f$ states of Sm in SmS under pressure.

ACKNOWLEDGMENTS

We thank J. Forstreuter, A. Mishchenko, A. F. Barabanov, R. Hayn, P. Soederlind, and C. Lehner for critical remarks and valuable discussion. The work was supported by the DFG Grant No. Re 1052/2-1.

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