

Valence State of the Sm Metal

Y. -R. Jang

Department of Physics, University of Incheon, Incheon 402-749, Korea

Byung Il Min

*Department of Physics, Pohang University of Science and Technology,
Pohang 790-784, Korea*

(Received 24 November 1997)

Valence state of the Sm metal is investigated using the total energy linearized muffin-tin orbital (LMTO) band method for the observed Sm-type crystal structure. We have considered both the relativistic and the semi-relativistic description of 4f-core electrons. We have found that, in the paramagnetic phase of bulk Sm, the trivalent valence state is more stable at the observed lattice constant than the divalent valence state.

1. Introduction

Rare earth (RE) metals are characterized by open 4f shells which give rise to a variety of interesting electronic and magnetic properties. Properties of RE elements and their compounds have been studied extensively over last decades. Of particular interest is the intermediate- or mixed-valence phenomena which has been observed in some RE compounds and alloys. In mixed-valence materials, two configurations $4f^{n+1}V^2$ (divalent) and $4f^nV^3$ (trivalent) (where V stands for the valence electrons) are so close in energy that the ground state has to be described quantum mechanically as a superposition of these two configurations.

Among the RE metals, compounds of Ce, Sm, Eu, Tm, and Yb possess the mixed-valence state [1]. In particular, Sm has some distinct characters, in that the other metals (Ce, Eu, Tm, and Yb) themselves have been considered to be in an integral-valence state. In contrast, X-ray photoemission spectroscopy (XPS) spectra [2] indicated that Sm is divalent in SmTe, trivalent in SmSb, mixed-valent in SmB₆, and also in Sm metal. Furthermore, Sm is the only pure metal known to have the Sm-type crystal structure [3].

A study of XPS spectra for the 4d electrons [4] has strongly suggested that either the bulk or the surface state of metallic Sm is in a mixed-valence state. It was also suggested [5] that the presence of the divalent peak in the XPS spectrum was exclusively a surface effect. In view of a surface-sensitivity in XPS measurements [6], it has been reported that Sm changes from being single valent in the bulk to inhomogeneously mixed valent

on the surface.

Existing calculations [7, 8] indicates that the trivalent state is energetically favored in bulk Sm. In these calculations, however, some simplifications were adopted: the renormalized atom method which is structure-independent [7], and the face-centered-cubic (fcc) structure which is one of close-packed structures [8]. Note that Sm crystallizes in its unique Sm-type structure.

In this paper, we have performed total energy band structure calculations for Sm with Sm-type structure considering different valence states. The outline of this paper is as follows. In section 2, we present briefly the methodology used in our calculation. In section 3, we discuss the results of total energy for some different cases and interpret these results in relation to the valence state of Sm metal. Finally, the conclusion follows in section 4.

2. Methods

To determine total energies of Sm metal, we have solved the one-particle Kohn-Sham (KS) equations [9, 10] within the local spin density approximation (LSDA) [11]. These equations are solved self-consistently by means of the linearized muffin-tin orbital (LMTO) band method [12]. We have employed the explicit form of von Barth-Hedin formula [13] for the local spin exchange-correlation potential. The tetrahedron scheme for the Brillouin zone integrations is utilized. Band calculations are performed over 60 k-points in the irreducible Brillouin zone.

We have performed the total energy band calculations for the following two different cases: (i) divalent (6 electrons in 4f core states and 2 in valence states) (ii) trivalent (5 in core and 3 in

valence). First, the core electrons are treated fully relativistically and the valence states are calculated semirelativistically, which means, we neglect the spin-orbit interaction for the valence states. This, however, may give rise to an inconsistency for the resulting total energy values, because in the former case two electrons are treated semirelativistically while in the latter three electrons are treated semirelativistically. In this sense, it is expected that the semi-relativistic treatment of both 4f core and valence electrons is more consistent than the relativistic one for the comparison of total energy values. Therefore, secondly, we have obtained the total energy considering eight (the sum of 4f core and valence) electrons semi-relativistically. We have also compared total energies between the paramagnetic (PA) state and the spin-polarized (SP) state.

3. Results and Discussion

Figure 1 displays the total energy curves for the divalent ($4f^6$ core configuration) and the trivalent ($4f^5$ core configuration) states versus lattice constant represented by the Wigner-Seitz radius R_{ws} . In Fig. 1, SR stands for the semi-relativistic calculation for eight (4f core and valence) electrons, R for the relativistic calculation for 4f core electrons, PA for the paramagnetic state, SP for the spin-polarized state, 2 for the divalent state, and 3 for the trivalent state, respectively. One can see that the spin-polarized states have lower energies than the paramagnetic ones in all cases, and the relativistic calculations have lower energies than the semi-relativistic ones. Figure 1 also

shows that the divalent case is energetically favored for the spin-polarized state both in the relativistic and the semi-relativistic treatments of 4f core electrons.

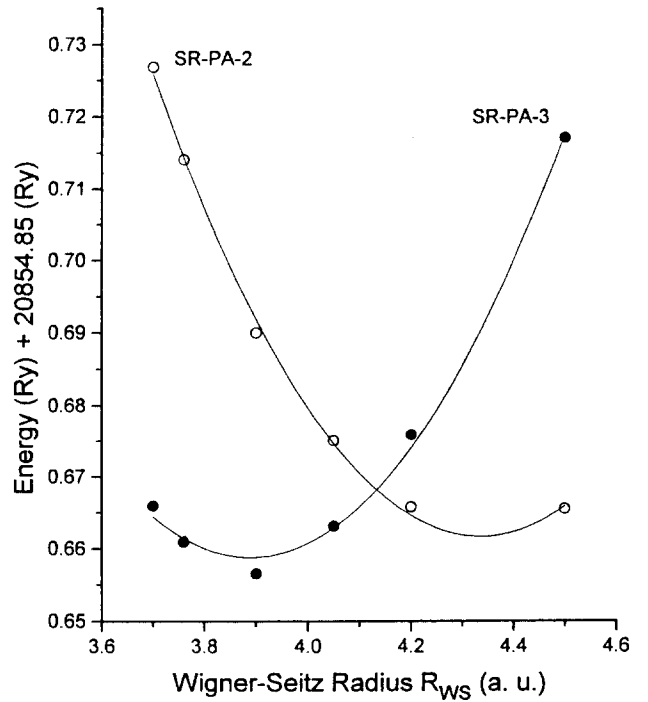


Fig. 2. Total energy for paramagnetic states using the semi-relativistic calculation.

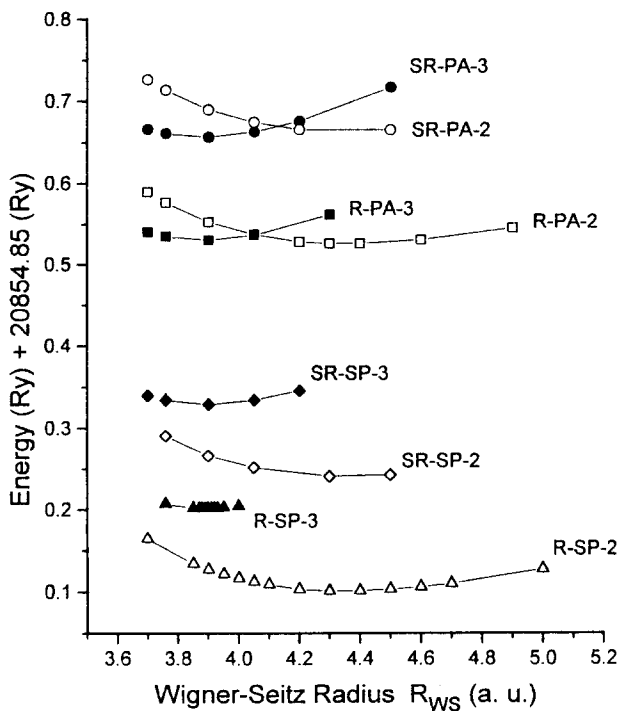


Fig. 1. Total energy versus lattice constant represented by the Wigner-Seitz radius R_{ws} .

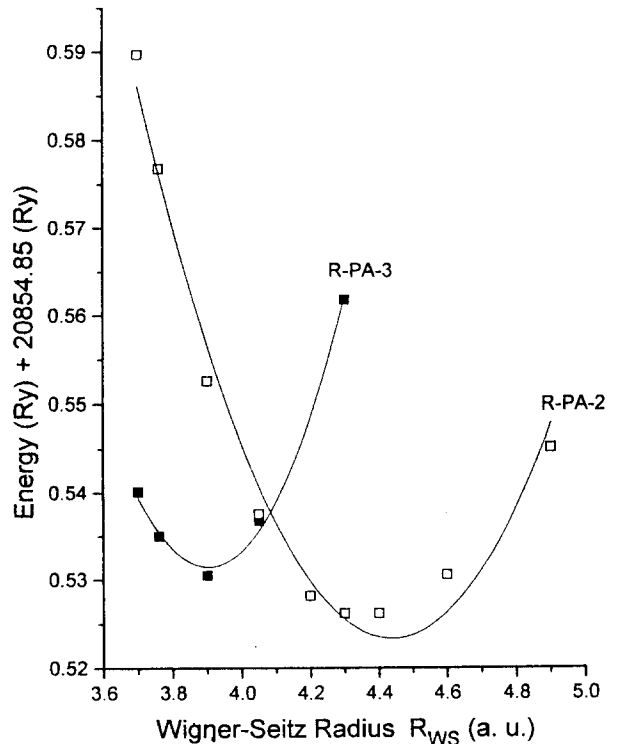


Fig. 3. Total energy for paramagnetic states using the relativistic calculation.

For paramagnetic cases, Fig. 2 and Fig. 3 show that the trivalent state is favored in the semi-relativistic treatment while the divalent is favored in the relativistic treatment. Therefore, the trivalent state is favored only for the paramagnetic state with the semi-relativistic calculation. In fact, the paramagnetic state is the ground state at room temperature. Hence, present results for the Sm-type structure seem consistent with the experimental facts. Furthermore, they are in agreement with previous calculations done for the assumed simple crystal structures [7, 8]

Using a numerical least-square fitting, we can find that the trivalent paramagnetic state with the semi-relativistic calculation has a minimum at $R_{ws}=3.89$ a.u., which is slightly larger than the observed value of $R_{ws}=3.76$ a.u. but smaller than the structure-independent calculation [7] (see Table I). For the divalent curve, we have also obtained slightly smaller values than Ref. 7. At the observed value of $R_{ws}=3.76$ a.u., both Fig. 2 and Fig. 3 give the trivalent paramagnetic state lower in energy than the divalent one.

Table 1. Calculated ground state properties of bulk Sm: R_{ws} denotes the equilibrium Wigner-Seitz radius in a.u., E_0 equilibrium total energy per atom (+ 20854.85) in Rydberg, and B bulk modulus in Mbar. See text for the notations of SR, R, PA

	R_{ws} (a.u.)	$E_0 + 20854.85$ (Ry)	B (Mbar)
trivalent (+3)			
SR-PA	3.889	0.6588	0.3164
R-PA	3.903	0.5315	0.3870
Ref [7]	3.92		0.37
Ref [16]	3.76		0.38
divalent (+2)			
SR-PA	4.337	0.6617	0.2852
R-PA	4.438	0.5234	0.2025
Ref [7]	4.61		0.12

Finally, it should be pointed out that the real ground state of Sm at low temperatures is not paramagnetic but complicated antiferromagnetic (AF) [15], which has very complex magnetic structure. Thus, for the better understanding of the real ground state of Sm in bulk or surface, more accurate calculations are required by taking into account explicitly both the real crystal and magnetic structures.

4. Conclusion

We have investigated the valence state of Sm metal, per-

forming the total energy LMTO band structure calculations. Considering 4f electrons as core, we have employed both the relativistic and the semi-relativistic treatment for core electrons. We have found that the paramagnetic phase of bulk Sm has the stable trivalent valence state at the observed lattice constant.

Acknowledgments

This work was supported in part by the 1996 Research Fund from the University of Incheon, by the Basic Science Research Institute Program, Ministry of Education, under Project No. BSRI-97-2448, and by the POSTECH-BSRI program (BSRI-97-2438) of the Korean Ministry of Education. Helpful discussions with Dr. Suk Ju Youn, Prof. J. I. Lee, Prof. S. C. Hong are greatly appreciated.

References

- [1] J. M. Lawrence, P. M. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).
- [2] S. P. Kowalczyk, N. Edelstein, F. R. McFeely, L. Ley, and D. A. Shirley, Chem. Phys. Lett. **29**, 491 (1974).
- [3] The ground state of Li is proposed to have a Sm-type crystal structure.
- [4] J. -N. Chazalviel, M. Campagna, G. K. Wertheim, and P. H. Schmidt, Solid State Commun. **19**, 725 (1976); Phys. Rev. B **14**, 4586 (1976).
- [5] G. K. Wertheim and M. Campagna, Chem. Phys. Lett. **47**, 182 (1977).
- [6] J. W. Allen, L. I. Johansson, I. Lindau, and S. B. Hagstrom, Phys. Rev. B **21**, 1335 (1980).
- [7] J. F. Herbst and J. W. Wilkins, Phys. Rev. B **24**, 1679 (1981).
- [8] S. C. Hong, J. I. Lee, Y. -R. Jang, B. I. Min, and A. J. Freeman, J. Magn. Magn. Mater. **104-107**, 659 (1992).
- [9] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [10] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [11] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
- [12] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
- [13] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
- [14] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).
- [15] W. C. Koehler and R. M. Moon, Phys. Rev. Lett. **29**, 1468 (1972).
- [16] T. E. Scott, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, p. 674.