PHYSICAL REVIEW B VOLUME 43, NUMBER 8 15 MARCH 1991-I

Ground-state properties of lanthanum: Treatment of extended-core states

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(Received 27 September 1990; revised manuscript received 19 November 1990)

Three related techniques for performing accurate electronic-structure and total-energy calculations for systems with extended, so-called semicore, states are described. Total-energy calculations performed using the three methods are reported for fcc lanthanum. The convergence properties and relative accuracies of the three techniques are discussed. They are found to yield results in good agreement with each other and consistent with the available experimental data when well-converged calculations are performed. Highly accurate calculations are reported for the bcc phase, using one of these techniques, and a prediction of the bcc-fcc energy difference is reported.

INTRODUCTION

The general or full-potential linearized-augmented-plane-wave (LAPW) method[1] has been used extensively for density-functional-based electronic-structure and total-energy calculations in solids. The method is among the most accurate generally applicable techniques for this purpose. However, it is not without certain shortcomings. These derive primarily from the linearization, and as such are common to other linearized methods such as the widely used linearized-muffin-tin-orbital (LMTO) method. Among these shortcomings, perhaps the most serious is the difficulty in accurately treating systems with extended, so-called semicore, states.[2,3] Examples of such systems are found among materials containing rare-earth or early transition-metal atoms.

In the LAPW method space is partitioned into two regions, the region inside nonoverlapping atom centered spheres and the remaining interstitial region. The basis functions, charge densities, and potentials are represented differently in the two regions. For the charge densities and potentials, plane-wave expansions are used in the interstitial region and unrestricted lattice harmonic expansions are used in the spheres. These expansions are completely general. Thus the errors resulting from them can be made arbitrarily small. The basis functions are given by

$$\varphi_i = \begin{cases} e^{i(\mathbf{k}+\mathbf{G}_i)\cdot\mathbf{r}}\ , & \mathbf{r}\in I \\ \sum\limits_{l,m} [a^i_{lm} u_l(r) + b^i_{lm} \dot{u}_l(r)] Y_{lm}(\hat{\mathbf{r}})\ , & \mathbf{r}\in MT \end{cases} \tag{1}$$

where I refers to the interstitial region and MT to the region inside a sphere. The radial functions $u_l(r)$ are solutions of the radial Schrödinger equation in the spherically averaged crystal potential at the linearization energy, E_l, while the $\dot{u}_l(r)$ are the derivatives with respect to E_l. The a and b coefficients are chosen to make the basis functions continuous and differentiable at the sphere boundaries. Provided that the E_l are chosen close to the band energy of interest, this is a very good basis. Moreover, it can be shown that the radial functions (and hence the LAPW basis functions) are orthogonal inside the spheres to any core state whose wave function vanishes on the sphere boundary. For atoms with semicore states, which extend beyond the sphere radius, the orthogonality of the basis functions to the semicore states is only approximate. As discussed in Refs. 2 and 3, in such systems pathological dependencies of the energies on the linearization energy may be encountered. This problem does not occur for E_l near the energy of the semicore state and a well-converged description of that state may be obtained with this choice. Such a choice also ensures that the valence bands will be orthogonal to the semicore level. This is an unsatisfactory option, however, since any valence bands with the same l character as the semicore level will be poorly described, because the LAPW basis is a good one only for eigenvalues near E_l. As E_l is raised towards the valence bands the basis will become poorer for the semicore state and consequently its eigenvalue(s) will increase. As some point its energy will overlap the valence-band energies (in this case the state is referred to as a ghost state), consequently preventing total-energy calculations from being performed. As E_l is further increased the orthogonality of the valence band to the semicore state will be increasingly degraded. This will be manifested in a lowering of the calculated eigenvalues and total energies *below* the correct values.

In the present paper three related techniques for circumventing the above difficulties are described. A series of calculations for fcc lanthanum are reported and, using these, the three approaches are compared.

The reason for my choice of lanthanum as a test material is twofold. First of all, as may be expected from its high compressibility and extended 5*s* and 5*p* semicore states, total-energy calculations for lanthanum show considerable sensitivity to the treatment of the semicore states.[4,5] Using the general potential LAPW method, Lu, Singh, and Krakauer found that the calculated bulk modulus changed by a factor of 2 when the 5*p* state was treated as a normal core state, while Temmerman and Sterne, using an LMTO method, found that the calculated static lattice parameter changed by 5.6% when the 5*p* state was "frozen." Thus it is apparent that an accurate treatment of these states is essential in calculating the structural properties of lanthanum. The second reason for our choice of lanthanum derives from its physical interest. This derives in part from lanthanum's role as a useful reference material for the $4f$ materials and in part from its unusual properties. For example, lanthanum is superconducting with a large pressure dependence of T_c and has two structural phase transitions as a function of temperature. In a recent general potential LAPW study in which the static properties of fcc and bcc lanthanum were calculated, the difference between the experimental and calculated lattice parameters was larger than that found in most other materials and the bcc-fcc energy difference was apparently in disagreement with experiment.[4] As part of this study, new calculations with more accurate treatments of the semicore states are reported and the discrepancy in the lattice parameters is resolved.

METHODS

As mentioned, three techniques for correcting the deficiencies of the LAPW method are used in this study. All of these were implemented as additions to an existing general potential LAPW code and as such retain many of the features of that method. Most importantly, all the calculations reported here were performed fully self-consistently without shape approximations in the charge densities or potentials. One of these methods (a super-linearized APW method, which will be denoted SLAPW-4 here) has been previously described and used in a calculation of the H-point phonon frequency in molybdenum.[3] This method works by generalizing the LAPW basis functions so as to incorporate sufficient variational freedom that both the valence and semicore states may be accurately treated in a single energy window (or panel). In particular, the SLAPW-4 technique involves a change of augmentation, so that the plane waves are matched onto a single $u_l(r)$ and $\dot{u}_l(r)$ exactly as in the LAPW method for all l except those for which there are semicore states ($l=0$ and 1 in the case of lanthanum). For those l for which there are semicore states, two $u_l(r)$ and the corresponding two $\dot{u}_l(r)$ functions are used with the two E_l being set in the valence band and the semicore "band," respectively. The four matching coefficients are determined by requiring continuity of the basis function and three derivatives at the sphere boundary. Because only a single window is used, orthogonality of the semicore and valence bands is assured.

While for a sufficiently large number of plane waves an SLAPW-4 calculation has at least as much variational freedom as a two window LAPW calculation, this is not the case for smaller numbers of plane waves. In particular, in order to achieve the same level of convergence as in the LAPW method a significantly larger number of basis functions is required. This is a result of the additional matching conditions and can be understood as follows. Consider the case of a state localized inside a sphere. In this case, with an LAPW basis the linear combination of plane waves making up the interstitial part of the wave function will have to reproduce the correct ratio of the derivative of the wave function to its value at the sphere boundary. With the SLAPW-4 basis second and third derivatives also need to be reproduced in order to obtain a converged result. This is a much more demanding condition. Thus it was of interest to investigate whether a more efficient basis with sufficient variational freedom to accurately include both semicore and valence states in a single energy window could be formed by relaxing the matching requirements of the SLAPW-4 basis.

The most obvious change to the SLAPW-4 basis is to remove the second $\dot{u}_l(r)$ function and with it one matching condition. In this approach (denoted SLAPW-3 in the following), the usual $u_l(r)$ and $\dot{u}_l(r)$ functions, evaluated with E_l in the valence-band region, are supplemented by a second $u_l(r)$ for the l of the semicore states. The three coefficients are determined by requiring continuity of the basis functions and two derivatives. While it is clear that this basis has at least as much variational freedom as an LAPW basis for the valence bands, it is less clear that it will be adequate for the semicore states. This is because it is unclear whether in practice a suitable linear combination of a $u_l(r)$ and $\dot{u}_l(r)$ evaluated at E_l in the valence region (typically 1 Ry or more above the semicore states) can provide the extra variational freedom which semicore $\dot{u}_l(r)$ provides in a two window LAPW calculation. One of the purposes of the present study is to investigate this issue. Other modifications of the LAPW augmentation are certainly possible. Some of them have been studied by other workers in order to improve the accuracy of calculations for valence states in systems without the semicore problem discussed above.[6-8]

Both the SLAPW-3 and SLAPW-4 basis sets, described above, incorporate the extra variational freedom inside the spheres which is needed to describe semicore states at the expense of requiring the plane waves to "work" harder. That is, the matching conditions are more stringent and as a result they may be expected to be less efficient than the LAPW method in the sense that a larger basis set will be required to achieve a given level of convergence. In the hope of circumventing this reduction in efficiency, a third basis set has been tried. This is a mixed-basis approach, consisting of the usual LAPW basis functions and localized orbitals of the l character of the semicore states. The localized orbitals consist of symmetrized linear combinations of the two $u_l(r)$ and the $\dot{u}_l(r)$ as in the SLAPW-3 basis with the particular linear combination chosen so that the localized orbital goes to zero with zero derivative at the sphere boundary. The symmetrization is performed for the following reason. In an LAPW basis the Hamiltonian and overlap matrices are real for systems whose space groups contain inversion symmetry. In practical calculations this fact is exploited yielding a substantial reduction in the amount of computation required. This property (real matrices) is retained only if appropriate linear combinations of local functions (i.e., involving structure factors) are used as basis functions. The symmetrized basis functions are linear combinations of the original local orbitals and span the same space. Therefore the symmetrization has no effect on the variational freedom. In systems which do not have inversion symmetry the matrices are Hermitian and in this case the above symmetrization is not needed.

Because this basis, denoted LAPW+LO in the following, and the SLAPW-3 basis use the same functions inside the spheres they will have the same variational freedom for sufficiently large basis sets. Of course for small numbers of plane waves both basis sets are poor. In the LAPW+LO case a minimal basis would yield wave functions composed of restricted linear combinations of radial functions which go smoothly to zero at the sphere boundary. The SLAPW-3 basis will also involve restricted linear combinations of radial functions which in this case match smoothly onto specific plane waves. The question then is how quickly these basis sets improve as the number of augmented plane waves is increased. In this regard, we note that in contrast to the SLAPW-3 basis, the LAPW+LO basis involves the same matching conditions as the usual LAPW basis, i.e., continuity of the basis functions and *one* derivative, and thus may be expected to converge with respect to basis-set size at the same rate as a standard LAPW basis. (N. B., the extra functions do not represent a significant increase, e.g., treating the 5*s* and 5*p* semicore states in lanthanum requires four local orbitals per atom as compared to 60–100 augmented plane waves.) This is confirmed by the results below which demonstrate the LAPW+LO basis does indeed converge more rapidly than the SLAPW-3 basis.

If the converged LAPW+LO basis (or equivalently a converged SLAPW-3 basis which as noted contains the same radial functions) was found to provide insufficient variational freedom for treating the semicore states in some system, the LAPW+LO approach could be generalized to yield the same variational freedom as converged calculations with the SLAPW-4 basis, by doubling the number of local orbitals. Specifically, additional localized orbitals consisting of linear combinations of the valence $u_l(r)$ and two $\dot{u}_l(r)$ functions would be added. However, since, as will be shown below, the SLAPW-3 basis seems to be adequate for lanthanum, this was not tried.

COMPUTATIONAL PARAMETERS

As mentioned, the three methods, used in the present work, have much in common with the general potential LAPW method. As in that method, space is divided into atom centered spheres and an interstitial region. In the present study a sphere radius $R_{MT}=3.3$ a.u. was used. The calculations for the valence and semicore states were performed self-consistently in a scalar relativistic approximation. It seems likely that the largest remaining source of error in the present treatment of the semicore states results from the neglect of spin orbit for the lanthanum 5*p* states. The core states were also treated self-consistently but in this case fully relativistically in an atomic approximation. In the present work the Hedin-Lundqvist form of the exchange-correlation potential[9] was used. The required Brillouin zone integrations were performed using 60 special **k** points[10] for the study of the relative convergence with respect to basis-set size of the three methods. These tests were perfomed for the fcc structure at a lattice parameter of 9.8 a.u. with plane-wave cutoffs ranging from $R_{MT}K_{\max}=7.0$ to 11.0. Based on this convergence study (see below) it was determined that well-converged total energies for lanthanum were attainable using a cutoff of $R_{MT}K_{\max}=10.0$ for the SLAPW-3 and SLAPW-4 methods and $R_{MT}K_{\max}=9.0$ for the LAPW+LO method.

Total-energy calculations were performed for fcc and bcc lanthanum using several Brillouin zone samplings. These included sets of up to 408 special **k** points. Based on these tests, it was determined that well-converged results could be obtained using 182 special **k** points for the fcc structure and 240 for the bcc structure. Accordingly, these sets were used with the plane-wave cutoffs, discussed above, for the calculations of the ground-state properties.

RESULTS

As mentioned, in order to study the relative convergence of the three basis sets discussed above, self-consistent calculations of the total energy of fcc lanthanum at a lattice parameter of 9.8 a.u. were performed as a function of the basis-set size. Within a general potential method, comparison of total energies from self-consistent calculations is a good test of the variational freedom of a basis set. This follows because the self-consistent solution of the Kohn-Sham equations is variational, i.e., the solution yields an extremum of the total-energy functional. (Comparison of individual eigenvalues in a fixed potential is also of interest, but can be misleading because under certain circumstances degrading a basis can result in a lowering of some eigenvalues. Specifically, this sometimes occurs for valence eigenvalues when the representation of semicore states is degraded.) The results of this test are shown in Fig. 1 and Table I. The lowest eigenval-

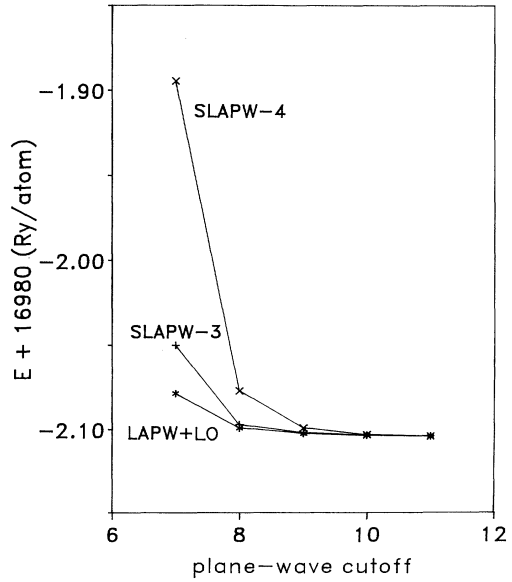

FIG. 1. Convergence of the SLAPW-3, SLAPW-4, and LAPW+LO basis sets (see text) with respect to plane-wave cutoff, $R_{MT}K_{\max}$. Shown are self-consistent total energies E for fcc lanthanum at a lattice constant of 9.8 a.u.

TABLE I. Calculated total energy E as a function of $R_{MT}K_{\max}$ for fcc lanthanum at a lattice parameter of 9.8 a.u.

		$E+16\,980$ Ry	
$R_{MT}K_{\max}$	SLAPW-4	SLAPW-3	LAPW+LO
7.0	$-1.894\,59$	$-2.049\,92$	$-2.078\,58$
8.0	$-2.076\,97$	$-2.097\,03$	$-2.099\,11$
9.0	$-2.098\,88$	$-2.101\,74$	$-2.102\,24$
10.0	$-2.102\,97$	$-2.103\,19$	$-2.103\,38$
11.0	$-2.103\,81$	$-2.103\,66$	$-2.103\,77$

TABLE III. Ground-state properties of fcc lanthanum. B is the bulk modulus, B' its pressure derivative, and a the equilibrium lattice parameter.

Technique	a (Å)	B (GPa)	B'
SLAPW-3	5.14	31.9	3.1
SLAPW-4	5.13	30.2	3.0
LAPW+LO	5.15	33.8	3.5
LAPW[a]	5.08	31.1	2.99
LMTO[b]	5.11	24.0	3.0
LMTO[c]	5.17	28.0	
Experiment[d]	5.304	24.8	2.8

[a] Reference 4.

[b] Reference 14.

[c] Reference 15.

[d] Room-temperature data (see text), Refs. 12 and 13.

ues at Γ for the three basis sets as a function of $R_{MT}K_{\max}$ in a fixed potential are given in Table II. For the chosen lattice parameter and sphere radius, the plane-wave cutoffs $R_{MT}K_{\max}=7.0$, 8.0, 9.0, 10.0, and 11.0 corresponded to a basis-set sizes of about (because of the discrete nature of the reciprocal lattice, the exact size depends on the particular **k** point in question) 45, 60, 75, 115, and 150, respectively, with the LAPW+LO basis sets being 4 larger than the SLAPW sets.

For all the basis-set sizes tested, except for the largest, the total-energy calculations show that SLAPW-4 was the least converged of the methods, while the LAPW+LO approach displayed the most rapid convergence. As discussed above, this may be expected for limited basis-set sizes, based on the number of matching conditions used in the three methods. On the other hand, for the largest basis set, the SLAPW-4 method yielded the lowest total energy, consistent with the extra variational freedom this basis has for large $R_{MT}K_{\max}$. This derives from the extra $\dot{u}_l(r)$ function. The fact that the converged total energies of the three methods (the LAPW+LO and the SLAPW-3 basis sets have the same converged total energy, though the LAPW+LO method converges more quickly) differ by much less than 1 mRy (extrapolating the results of Table I, about 0.05 mRy) is an indication that, at least in the case of lanthanum, the extra variational freedom of the SLAPW-4 method is unlikely to have a significant effect on the calculated properties. This is confirmed by the calculations of the static properties of fcc lanthanum using the three approaches. The trends discussed above are also reflected in the convergence of the eigenvalues (see Table II).

The static properties of fcc lanthanum were obtained by performing well-converged (see above) total-energy calculations for eight lattice parameters in the range 9.4 to 10.1 a.u. The total energies for lattice parameters between 9.5 and 10.0 a.u. (better fits were obtained by restricting the range of lattice parameter) were then fit to the Murnaghan equation of state.[11] The results of these fits are given in Table III along with room-temperature experimental data[12,13] and the results of previous LAPW and LMTO studies. As may be noted from Table III, the SLAPW-3, SLAPW-4, and LAPW+LO methods yield results in good agreement with each other. Based on the convergence test described above (i.e., the energies in Table I), for the particular choices of $R_{MT}K_{\max}$ made, the results obtained using the LAPW+LO method are somewhat less well converged than the SLAPW-3 results. The calculated lattice parameter is somewhat more than 1% larger than found using the LAPW method[4] and lies between the results of two LMTO studies which differ between themselves by about 1%.[14,15]

Since fcc lanthanum is not stable at low temperatures, no low-temperature experimental data are available. Thus while the room-temperature data given in Table III appear to be in only fair agreement with the present calculation, caution is required. A better estimate of the static lattice parameter can be obtained extrapolating from room temperature using experimental data for the thermal expansion.[13] In lanthanum the variation of the atomic volume of the low-temperature double hcp (dhcp) phase and the fcc phase is almost parallel in the range of

TABLE II. Calculated eigenvalues at Γ as a function of $R_{MT}K_{\max}$ for fcc lanthanum at a lattice parameter of 9.8 a.u. These non-self-consistent calculations were performed using a converged SLAPW-4 potential. The eigenvalues (given in Ry) are with respect to the average interstitial potential. (For a converged calculation this is 0.473 Ry below the Fermi energy.)

		$5p$			Γ_1	
$R_{MT}K_{\max}$	SLAPW-4	SLAPW-3	LAPW+LO	SLAPW-4	SLAPW-3	LAPW+LO
7.0	$-0.543\,23$	$-0.651\,06$	$-0.669\,99$	$0.241\,31$	$0.236\,38$	$0.236\,11$
8.0	$-0.671\,79$	$-0.673\,12$	$-0.673\,38$	$0.236\,29$	$0.236\,06$	$0.236\,07$
9.0	$-0.672\,61$	$-0.673\,26$	$-0.673\,38$	$0.236\,13$	$0.236\,06$	$0.236\,06$
10.0	$-0.673\,40$	$-0.673\,46$	$-0.673\,47$	$0.236\,07$	$0.236\,05$	$0.236\,05$
11.0	$-0.673\,51$	$-0.673\,51$	$-0.673\,51$	$0.236\,06$	$0.236\,05$	$0.236\,05$

coexistence, while both of these curves are quite featureless. Thus the fcc static lattice parameter may be estimated by assuming that the (hypothetical) fcc atomic volume shows the same variation as the dhcp volume down to 0 K. Making this assumption, a lattice parameter of 5.20 Å is obtained, in very good agreement with the present results. While the calculated bulk modulus is significantly larger than the room-temperature experimental value, it is difficult to determine to what extent this difference is due to a reduction in the experimental value due to thermal effects. The close agreement between the extrapolated experimental lattice parameter and the calculated lattice parameter is an indication that the apparent disagreement with experiment may be misleading.

fcc lanthanum is thermodynamically unstable at elevated temperatures, and transforms to a bcc phase at about 1140 K. Lu, Singh, and Krakauer have performed general potential LAPW calculations of the static properties of lanthanum in this structure as well as the bcc-fcc energy difference.[4] The calculated energy difference was 11.5 mRy per atom. This is considerably larger than the 5 mRy estimated from experimental data by Jayaraman.[16] Thus it was of interest to determine whether this discrepancy could be resolved using the present treatment of the semicore states. Accordingly, SLAPW-4 calculations of the static properties of bcc lanthanum and the bcc-fcc energy difference were performed. The results of these calculations are shown in Table IV. Except for a 1.5% increase in the lattice parameter, consistent with the results for the fcc structure, the present results are in good agreement with the LAPW results. In particular, the calculated fcc-bcc energy difference is 11.4 mRy/atom, which is practically identical to the 11.5 mRy/atom obtained with the LAPW method. It seems that a reexamination of the experimental data may be worthwhile.

TABLE IV. Calculated static lattice ground-state properties of bcc lanthanum. ΔE denotes the bcc-fcc energy difference.

Technique	a (Å)	B (GPa)	B'	ΔE (mRy/atom)
SLAPW-4	4.13	32.9	3.0	11.4
LAPW[a]	4.07	31.1	2.9	11.5

[a] Reference 4.

CONCLUSIONS

Three related techniques for performing accurate total-energy and electronic-structure calculations for materials with semicore states have been described. Calculations have been presented for fcc lanthanum using the three techniques and for bcc lanthanum using one of them. It is found that the bcc-fcc energy difference is practically identical to that calculated using the LAPW method, but that the lattice parameters are somewhat larger.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Office of Naval Research. Computations were performed at the Cornell National Supercomputer Facility. I am grateful for several stimulating conversations with Dr. Dale Koelling.

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[1] O. K. Andersen Phys. Rev. B **12**, 3060 (1975); D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981); S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); S. -H. Wei, H. Krakauer, and M. Weinert, Phys. Rev. B **32**, 7792 (1985).

[2] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **33**, 823 (1986).

[3] D. Singh and H. Krakauer, Phys. Rev. B **43**, 1441 (1991).

[4] Z. W. Lu, D. Singh, and H. Krakauer, Phys. Rev. B **39**, 4921 (1989).

[5] W. M. Temmerman and P. A. Sterne, J. Phys. Condens. Matter **2**, 5529 (1990).

[6] T. Takeda and J. Kubler, J. Phys. F **9**, 661 (1979).

[7] L. Smrcka, Czech J. Phys. B **34**, 694 (1984); J. Petru and L. Smrcka, *ibid.* **35**, 62 (1985).

[8] D. J. Shaughnessy, G. R. Evans, and M. I. Darby, J. Phys. F. **17**, 1671 (1987).

[9] L. Hedin and B. I. Lundqvist, J. Phys. C. **4**, 2064 (1971).

[10] A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5188 (1976); **16**, 1748 (1977).

[11] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[12] K. Syassen and W B. Holzapfel, Solid State Commun. **16**, 553 (1975).

[13] Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, Thermophysical Properties of Matter (Plenum, New York, 1975), Vol. 12, pp. 173–175.

[14] D. Glotzel, J. Phys. F **8**, L163 (1978).

[15] A. K. McMahan, H. L. Skriver, and B. Johansson, Phys. Rev. B **23**, 5016 (1981).

[16] A. Jayaramen, Phys. Rev. **139**, A690 (1965).