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High pressure structural phase transitions in Sr from *ab initio* calculations

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The pressure-induced phase transition in strontium, including the recent experimental observation of high-pressure phase Sr-IV, was investigated theoretically using the projector augmented wave method. We also concentrated on the experimentally observed β-tin structure as this structure has never been found in any other alkaline-earth metals. The fcc-bcc phase transition was reproduced, but Sr-IV was found to be energetically more stable than the β-tin structure at all pressures. By considering enthalpy, the sequence of the phase transitions along the pressure range is $fcc \rightarrow bcc \rightarrow$ Sr-IV. With some detailed examination, we concluded that the β-tin structure is either a metastable state or a coexisting phase, and further experimental investigation is suggested.

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I. INTRODUCTION

Previous studies have shown that Sr undergoes structural phase transitions to several phases under high pressure. Based on experimental evidence, Sr is known to have a face-centered cubic (fcc) structure at ambient conditions and transforms to a body-centered cubic (bcc) structure at 3.5 GPa.[1] On further compression, there are phase transitions to Sr-III at 26 GPa, to Sr-IV at 35 GPa, and to Sr-V at 46 GPa.[1] The driving force for these crystallographic changes of Sr and also the other alkaline-earth metals is due to the transfer of electrons from *s*-*p* to *d* character.[2,3]

At the early stage, the structure of Sr-III was believed to be a distorted simple cubic[1] and later was claimed to be an orthorhombic structure.[4] However, Allan *et al.*[5] proposed a different interpretation of the Sr-III structure. From their report, the two-dimensional images obtained from an image plate (IP) revealed two different types of Debye–Scherrer rings—smooth rings and spotty rings. It is important to note that this texture information, which was obtained from the two-dimensional diffraction data, cannot be detected by energy dispersive techniques and hence would not have been observed previously. This two-dimensional image clearly distinguishes the majority phase spotty lines from the formation of an additional smooth phase accompanying the Sr-II to Sr-III transition. The smooth phase first manifests itself close to the $bcc \rightarrow \beta$-tin transition from a contaminant free "clean" bcc pattern. As the pressure is increased, the "low-pressure smooth phase" appears to have similar compressibility to Sr-III and it persists up to and through the Sr-III → Sr-IV → Sr-V transitions.[6] This "low-pressure smooth phase" is stable up to 57 GPa, at which it starts to transform to a "high-pressure smooth phase." This high-pressure smooth phase persists up to 75 GPa, the highest pressure ever reached in experimental studies. Upon pressure decrease, the diffraction pattern from the low-pressure smooth form progressively weakens until, at about 10 GPa, only a clean bcc pattern remains. These reported behaviors suggested that this smooth phase is another high-pressure structure of Sr, which so far has not yet been identified. The more recent experimental work by Bovornratanaraks *et al.*[6] have found that if the smooth phase is excluded, Sr-III is tetragonal, with the β-tin structure.

The structure of Sr-IV is rather complex and had long been unsolved.[1] The recent experimental observation[6] showed the Sr-IV structure as a monoclinic structure with the *Ia* space group and 12 atoms per unit cell. This structure can be considered as a helical distortion of the β-tin structure. The structure is even more complex in Sr-V, which was found to be a host-guest structure similar to that of Ba-IV.[7]

On the theoretical side, previous calculations[2,8–10] on the fcc-bcc phase transition found that the transition pressure is in reasonable agreement with the experiment. Ahuja *et al.*[3] studied the Sr-III phase using the FPLMTO method. This method gives an accurate description of the core structure and has no restriction on the core symmetry. They concluded that both base-centered orthorhombic (bco) and β-tin structure could be found in experiment. They also predicted the transition pressure for the bcc to bco to be around 40 GPa.

It is worth mentioning here that the β-tin structure has never been observed in any phase of other alkaline-earth metals.[11] Nevertheless, Katzke and Toledano[11] showed that the structures of β-tin, Sr-IV, and Sr-V are closely related, i.e., only small atomic movements within a common minimal supercell are required. Furthermore, they also showed that there is no simple transformation path from bcc to Sr-IV unless it passes some intermediate phases, such as β-tin or other complex structures with an orthorhombic $C222_1$ symmetry.

In this work, we attempt to reproduce the experimentally proposed phase diagram of Sr under pressure using a standard *ab initio* method, and we examine the existence of the β-tin structure in some detail as it has been a controversial subject.

II. CALCULATION DETAILS

The present calculations have been done using the projector augmented wave (PAW) method, as implemented in VASP 4.6 code.[12,13] The PAW potentials[14,15] used in the calculation treat 4*s*, 4*p*, and 5*s* states as valence states. The pseudocore radius is 2.50 bohr, which is small enough that the overlap of spheres will not occur. The generalized-gradient approximation (GGA) functional of Perdew–Wang, 1991,[16] was adopted for the exchange-correlation energy. We also tried Perdew-Burke-Ernzerhof (PBE) functionals[17] in the calculations, but the general conclusions are still the same.

The stability of high-pressure phases was considered from the enthalpy, $H=E+PV$, for a given pressure. The procedure is based on optimizing the structure at fixed volumes and fitting a Birch–Murnaghan equation of state (EOS). The energy curves were calculated for a number of volumes for each crystal structure, and the bulk modulus and its pressure derivative were obtained from the EOS. For all phases, geometry optimizations at constant volumes were performed for at least ten different volumes. Geometry optimizations were done using a standard conjugate gradient minimization algorithm. The optimization is converged when the energy difference between steps is less than 0.1 meV.

The total energy calculations were carried out using a cutoff energy of 500 eV. We found that increasing the energy cutoff to 700 eV makes the differences in absolute energy less than 1 meV. Sampling of the irreducible Brillouin zone was chosen according to Monkhorst–Pack scheme, with 195 *k* points for bcc and fcc, 168 *k* points for β-tin, and 60 *k* points for Sr-IV. These *k*-point samplings gave the total energy convergence within 1 meV. The cutoff energy and *k*-point grid were kept fixed throughout the calculations to avoid discontinuity in the total energy curve.

III. RESULTS AND DISCUSSION

In order to verify our calculations, the phase stability and structural properties of the well-studied phases, such as fcc and bcc, are considered in some detail. Our calculations correctly predict the fcc structure at 0 K and in absence of pressure. The fcc has only slightly lower energy than that of the bcc by 0.006 eV/atom. The whole energy-volume curves of both phases are comparable to the results from FPLAPW.[8] This shows the compatibility between the full-potential core and the pseudocore of this system. The calculated structural parameters along with the previous theoretical and experimental data are summarized in Table I. The calculated lattice parameters and the bulk moduli are in very good agreement with the previously reported data, except the experimental bulk modulus of the bcc phase which was measured at 930 K. This exhibits sufficient transferability of the potential and also reliability of our calculations.

Next, we perform the *ab initio* calculations of the β-tin [Fig. 3(a)] and Sr-IV structures [Fig. 3(c)]. The comparison of calculated pressure-volume relations with some experimental data are shown in Fig. 1. The results for the fcc phase agree very well with the experiment. For the Sr-IV phase, the calculated pressures are larger by about 4 GPa. We found the volume reduction for bcc to β-tin to be 3.7% compared to the experimental result of 1.7%.[4]

TABLE I. The calculated structural parameters for the fcc and bcc phases, compared to the previous theoretical and experimental results.

Phase	Pressure	a (Å)	B_0 (Mbar)	Method
fcc	0 GPa	6.010	0.117	This work
		6.052	0.110	FPLAPW-GGA[a]
		6.086		Expt.[b]
		6.076		Expt.[c]
			0.115	Expt.[d]
bcc	4.2 GPa	4.378	0.116	This work
		4.378	0.112	FPLAPW-GGA[a]
		4.434		X ray[e]
			0.088	Neutron (930 K)[f]

[a] Reference 8.
[b] Reference 18.
[c] Reference 19.
[d] Reference 20.
[e] Reference 21.
[f] Reference 22.

In Fig. 2, we show the difference in the enthalpy as a function of pressure. The enthalpy of the bcc structure is chosen as the zero-reference level. A crossing between any two curves indicates a pressure-induced phase transition. With increasing pressure, we find that Sr transforms from the fcc phase to the bcc phase. The transition occurs at 1 GPa, which is below the experimental observation of 3.5 GPa.[1] The underestimation of the fcc-bcc transition pressure by our calculations is similar to the previous calculation by Jona and Marcus.[8] They also showed that including the zero-point motion energy only slightly improves the transition pressure.

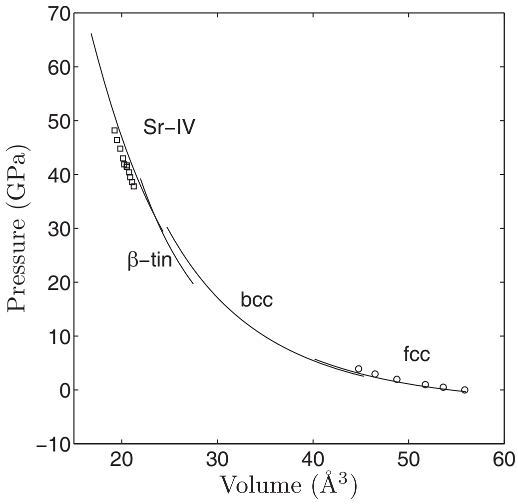


FIG. 1. The equation of states of the different phases of Sr. The circles label the experimental data for the fcc phase (Ref. 9) and the squares label the experimental results of the Sr-IV phase (Ref. 6). The solid line corresponds to the results from fitting to the Birch–Murnaghan equation of states.

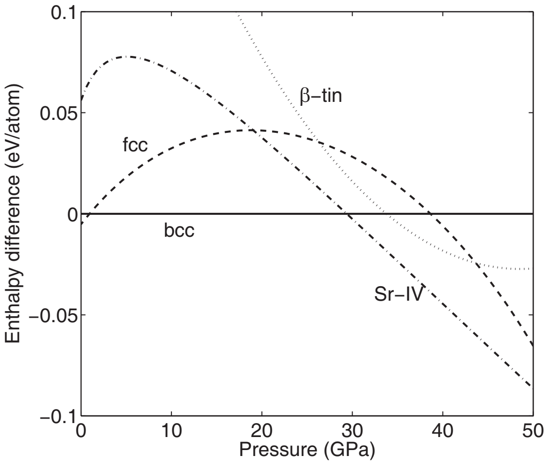


FIG. 2. The difference in the enthalpy between the bcc, fcc, β-tin, and Sr-IV phases as a function of pressure. The enthalpy of the bcc structure is chosen as the zero-energy reference level.

At higher pressure, we find that Sr-IV has lower enthalpy than that of β-tin for the whole pressure range. Thus, the β-tin structure is energetically unfavorable. This means that Sr should go directly from the bcc to the Sr-IV phase at 30 GPa. This is inconsistent with the experiment, where the bcc undergoes phase transformation to the β-tin at 26 GPa and then to Sr-IV at 35 GPa. However, the agreement with the experiments in terms of the structural parameters of the β-tin unit cell is excellent (see Table II). This attracted our attention. It could be that the β-tin is a metastable state or a coexisting phase, as suggested by experiment. If we consider only the transition between the bcc and β-tin, the transition takes place at 34 GPa, compared with 40 GPa calculated by Ahuja *et al.*[3] using the FPLMTO method. We have tried the bco structure also, and we found that its enthalpy is slightly larger than β-tin's.

Now, as the existence of the pure β-tin structure becomes questionable, it needs careful consideration. As the results from the pseudocore potential and the full potential are similar, hence, the core properties are irrelevant for the accuracy or the description of the system. We examine whether the accuracy of our calculation is insufficient and might lead to the inconsistency. This is because the energy difference between the β-tin and the Sr-IV is very small. In order to improve the calculation accuracy, we use unit cells of the same size between the two phases, as their unit cells are closely related to each other. The β-tin structure can be constructed by placing three Sr atoms at the 4a sites of the Ia unit cell at $u_1=(1/3,1/8,2/3)$, $u_2=(1/2,5/8,1/2)$, and $u_3=(2/3,1/8,1/3)$ and by fixing $a=c$, [Fig. 3(b)]. Therefore, both phases can be calculated under the same computational setting, and systematic errors tend to cancel. Even so, the calculations of the β-tin with the Sr-IV setting still give the same answer, i.e., the Sr-IV has lower energy than that of the β-tin for all pressures.

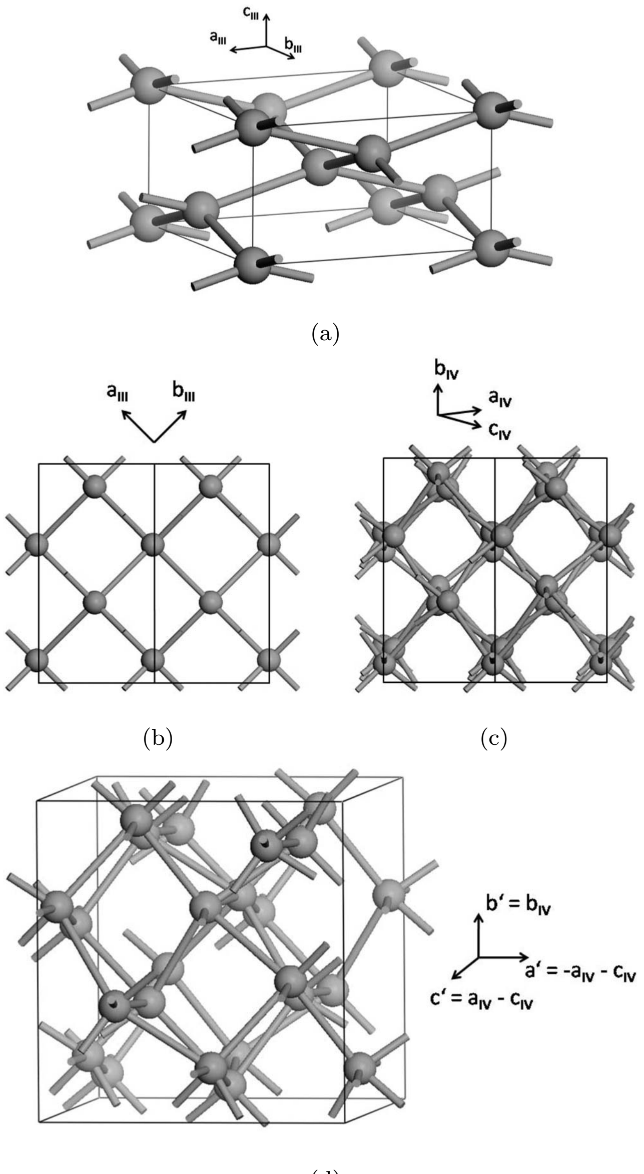
At this stage, we concentrate on the β-tin structure. According to Ref. 11, the bcc and the β-tin structures are related and, also, β-tin is closely related to Sr-IV. However, there is no simple transformation path from bcc directly to Sr-IV. In terms of the energy landscape, this implies that the potential barrier between bcc and Sr-IV must be very large. Thus, under the phase transition, it needs to pass through an alternative path. In order to prove this, we enlarge our simulation cell so that it can relax the symmetry constraint. By simply doubling the Sr-IV unit cell, it leads to a conventional cell of 24 atoms [Fig. 3(d)] and is similar to the orthorhombic $C222_1$ symmetry of the Rb-III.[11] This pseudo-othorhombic cell is very important because it coincides with the maximal substructure common to β-tin, Sr-IV, and Sr-V structures, and hence allows the structure to transform to any of these three structures.

By setting several unit cell sizes, we perform full relaxation of the pseudo-orthorhombic structure. The cell shape and the atomic positions are allowed to move with only constraint on fixed volume. The relaxation of the pseudo-orthorhombic cells is performed with two different initial geometries. One corresponds to the atomic positions of the β-tin structure, and we label it as the "β-tin setup." The other corresponds to the Sr-IV structure, we label it as the "Sr-IV setup." The calculations were done using a plane wave cutoff of 300 eV, and the k-point sampling is $3\times3\times2$ for the geometry optimization and $6\times6\times4$ for the static energy calculations. It is widely known that the minimization algorithm used in the relaxation process only takes the system to its nearest local minimum. So, if β-tin is unstable, it should transform to other structures under the relaxation process.

The results of the energy-volume curve of the pseudo-orthorhombic cell with the β-tin and the Sr-IV setups are shown in Fig. 4. There is a crossing between these two energy curves at the volume around 28 Å^3, which corresponds to the pressure of about 20 GPa. However, by analyzing the resulting structure, we find that the symmetry of these structures has changed. As displayed in the table in Fig. 4, the space group of the β-tin setup, which has a volume larger

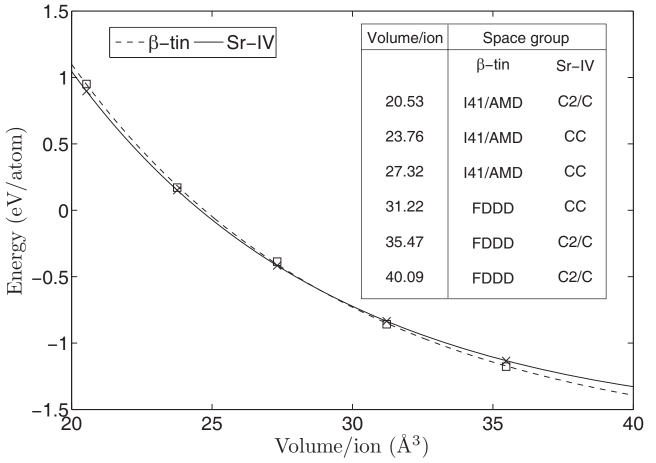
TABLE II. The structural parameters of β-tin and Sr-IV structures under pressure compared to the experimental observation. The numbers in the parentheses are experimental data from Bovornratanaraks *et al.* (Ref. 6).

		Lattice parameters (Å)			Angle (deg)	Internal coordinates			
Phase	Pressure (GPa)	a	b	c	β		x	y	z
β-tin	37.9 (34.8)	5.464 (5.504)	5.464 (5.504)	2.975 (2.960)	90.0 (90.0)	u	0.000 (0.000)	0.500 (0.500)	0.025 (0.025)
Sr-IV	45.9 (41.7)	5.705 (5.746)	8.053 (7.801)	5.331 (5.537)	98.1 (97.1)	u_1	0.280 (0.304)	0.152 (0.157)	0.600 (0.632)
						u_2	0.489 (0.479)	0.565 (0.578)	0.481 (0.465)
						u_3	0.698 (0.684)	0.152 (0.145)	0.362 (0.346)



(d)

FIG. 3. (a) The structure of β-tin in conventional cell. (b) The β-tin in Sr-IV unit cell, viewed along the *c*-axis direction. (c) The Sr-IV structure. For (b) and (c), the solid line represents the Sr-IV unit cell. (d) The pseudo-orthorhombic superstructure and the relationship between the unit cell of Sr-IV phase and the pseudo-orthorhombic.



Volume/ion	Space group	
	β–tin	Sr–IV
20.53	I41/AMD	C2/C
23.76	I41/AMD	CC
27.32	I41/AMD	CC
31.22	FDDD	CC
35.47	FDDD	C2/C
40.09	FDDD	C2/C

FIG. 4. The total energy as a function of volume of the β-tin and the Sr-IV setups in the pseudo-orthorhombic conventional cells. The inset table shows the space group of the relaxed structure for each volume.

than 28 Å^3, becomes *Fddd* rather than $I4_1/amd$. Surprisingly, this means that the β-tin setup tends to transform to a bcc-like structure, which is the stable phase in that pressure range. On the other hand, it is stuck in the β-tin structure under the Sr-IV pressure. For the Sr-IV setup, it stays as the Sr-IV for all pressures. This leads us to conclude that the β-tin structure is unstable in the bcc pressure, but it is a metastable state in the Sr-IV pressure.

We arrive at two extreme scenarios. First, if Sr-III is not the β-tin structure, as suggested by the enthalpy calculations, we need more information from repeated experiments in order to obtain a more accurate structure solution. Second, if Sr-III is the β-tin structure, as discussed above, it has high possibility that it is a metastable state or a coexisting structure with an unsolved smooth phase. This unsolved smooth phase was detected by experiments.[4–7] However, in the diffraction pattern, there were too weak and too fewer peaks to obtain a reliable structure solution. Nevertheless, the diffraction pattern did suggest that the smooth phase is from very small randomly oriented grains with a certain crystal structure. From a theoretical point of view, structures with the lowest energy are possible candidates. The strongest candidate in this pressure range is a base-centered orthorhombic structure, as it has energy close to β-tin.[3] By symmetry consideration, an orthorhombic $C222_1$ structure is also possible.[11] An experimental investigation suggested that Sr-III could be the β-tin structure with minor orthorhombic distortion.[4]

The role of this minority phase requires further investigation. We propose a few suggestions here; first, the volume reduction at the bcc to β-tin transition from our calculation is about 3.7%, consistent with the experimental result of 1.7% by Winzenick and Holzapfel.[4] The minority phase would compensate for this little volume change during the phase transition. Second, as Sr-V is an incommensurate structure where the same type of atoms exhibits different electronic and structural properties, i.e., a host-guest structure. It would be possible that the minority phase is a precursor to the commensurate-incommensurate phase transition. This behavior was found in other elements, such as Ba,[7] as well. An experiment with a strong x-ray intensity, like a synchrotron source, will help clarify these points and perhaps give more insight information of the role of the smooth phase. Also, *in situ* heating might help identify the metastable states.

IV. CONCLUSION

In this study, we have investigated theoretically the pressure-induced phase transformations in Sr up to 50 GPa. The calculations reproduce the fcc and bcc phases, and the transition pressure is at 1 GPa, comparable to the observed transition pressure. The calculated results also predict that the Sr-IV is more stable than the pure β-tin structure. By considering the enthalpy alone, the bcc phase should go directly to the Sr-IV phase at 30 GPa. However, the calculated atomic positions of the β-tin structure are in excellent agreement with experimentally derived results. Then we enlarged the simulation cell so that it could accommodate the β-tin, Sr-IV, and Sr-V geometries. We obtained evidence that indicates that pure β-tin is unstable in the bcc pressure but is a plausible structure in the Sr-IV pressure. If we take into account the reported observation of the smooth accompanying phase that occurs instantly with the transition from Sr-II to Sr-III structure, we should be able to conclude that the pure β-tin structure is not a stable structure for Sr-III but there must be a coexisting phase along with another unknown structure.

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[1] H. Olijnyk and W. B. Holzapfel, Phys. Lett. **100A**, 191 (1984).

[2] H. L. Skriver, Phys. Rev. Lett. **49**, 1768 (1982).

[3] R. Ahuja, B. Johansson, and O. Eriksson, Phys. Rev. B **58**, 8152 (1998).

[4] M. Winzenick and W. B. Holzapfel, Phys. Rev. B **53**, 2151 (1996).

[5] D. R. Allan, R. J. Nelmes, M. I. McMahon, S. A. Belmonte, and T. Bovornratanaraks, Rev. High Pressure Sci. Technol. **7**, 236 (1998).

[6] T. Bovornratanaraks, D. R. Allan, S. A. Belmonte, M. I. McMahon, and R. J. Nelmes, Phys. Rev. B **73**, 144112 (2006).

[7] M. I. McMahon, T. Bovornratanaraks, D. R. Allan, S. A. Belmonte, and R. J. Nelmes, Phys. Rev. B **61**, 3135 (2000).

[8] F. Jona and P. M. Marcus, J. Phys.: Condens. Matter **18**, 4623 (2006).

[9] R. H. Mutlu, Phys. Rev. B **54**, 16321 (1996).

[10] V. L. Sliwko, P. Mohn, K. Schwarz, and P. Blaha, J. Phys.: Condens. Matter **8**, 799 (1996).

[11] H. Katzke and P. Toledano, Phys. Rev. B **75**, 174103 (2007).

[12] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[13] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[14] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[15] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[16] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[18] J. Donohue, *The Structure of the Elements* (Wiley, New York, 1974).

[19] W. B. Pearson, *A Handbook of Lattice Spacing and Structures of Metals and Alloys* (Pergramon, Oxford, 1967), Vol. 2.

[20] E. A. Brandes and G. B. Brook, *Smithells Metals Reference Book*, 7th ed. (Butterworth-Heinemann, Oxford, 1992).

[21] D. McWhan and A. Jayaraman, Appl. Phys. Lett. **3**, 129 (1963).

[22] J. Mizuki and C. Stassis, Phys. Rev. B **32**, 8372 (1985).