

Determination of the Structural Parameters of an Incommensurate Phase from First Principles: The Case of Sc-II

Sergiu Arapan,^{1,2,*} Natalia V. Skorodumova,¹ and Rajeev Ahuja^{1,3}

¹*Division of Materials Theory, Department of Physics and Materials Science, Uppsala University, Box 530, S-751 21 Uppsala, Sweden*

²*Institute of Electronic Engineering and Industrial Technologies, Academy of Sciences of Moldova, Academiei 3/3, MD-2028 Chişinău, Moldova*

³*Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden*

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We propose a procedure to accurately describe the structural parameters of an incommensurate phase using *ab initio* methods by approximating it with a set of analogous commensurate supercells. We apply this approach to obtain the structural parameters of the Sc-II phase, which has recently been identified as a complex incommensurate structure similar to Sr-V. The calculated incommensurate ratio γ , lattice parameters, and Wyckoff positions of Sc-II are in excellent agreement with the available experimental data. Our results show that γ increases with pressure up to 60 GPa approaching but never reaching the commensurate value $4/3$. Hence calculations do not confirm the prediction made based on the reanalyzing of experimental data. When pressure exceeds 70 GPa, γ shows a sharp decrease that might be considered as the precursor of a new structural phase transition.

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The high-pressure Sc-II phase was first observed in the study of the superconducting properties of Sc under pressure [1], where high-pressure resistivity measurements revealed the presence of resistance anomalies at around 17 GPa, accompanied by the onset of superconductivity and a progressive increase of the transition temperature under pressure. Later, energy-dispersive x-ray diffraction experiments showed that at 20 GPa Sc undergoes a structural phase transition [2]; however, the exact structure of this high-pressure phase remained a puzzle for more than two decades. None of the known crystal structures could fit the x-ray diffraction pattern of Sc-II [2–4]. Neither Sc followed the high-pressure transformation sequence $hcp \rightarrow \alpha Sm \rightarrow dhcp \rightarrow fcc$ predicted by canonical band-theory calculations for the rear-earth elements [5] and experimentally confirmed for Y and La [6]. Only with the recent advance in high-pressure characterization techniques, which led to the discovery of many new complex phases for the elements of the periodic table at high pressure [7–11], has the structure of Sc-II been identified as being built of two interpenetrating substructures with the incommensurate (IC) periods of translation along the c axis [12,13]. Initially, the complex Sc-II phase was resolved within the superspace group $I'4/mcm(00\gamma)$ and described as a composite structure comprising IC body-centered tetragonal (bct) host and guest cells [12]. The Sc-II phase was found to be stable from 22 up to 104 GPa [14] with $\gamma = c_1/c_2$ (1—host, 2—guest) increasing with pressure in the interval: $1.5 < \gamma < 1.6$ [12]. This solution, however, turned out to give too short guest-guest distances along the chains, and a new IC composite crystal structure, composed of a bct host and C -face-centered tetragonal (C fct) guest lat-

tices, has been proposed for the Sc-II phase [13]. This new solution describes the Sc-II phase by the superspace group $I4/mcm(00\gamma)$ with $\gamma = 1.2804$ at 23 GPa. The earlier *ab initio* calculations of two commensurate analogous supercells modeling $I'4/mcm(00\gamma)$ and $I4/mcm(00\gamma)$ structures [15] have shown that the solution suggested by McMahon *et al.* [13] is the stable structure of Sc above 20 GPa. Thus, Sc-II is found to be isostructural with Sr-V [superspace group $I4/mcm(00\gamma)$], although its structural parameters are closer to those of Bi-III and Sb-II [superspace group $I'4/mcm(00\gamma)$]. It also comes out that if the pressure dependence of γ for the $I'4/mcm(00\gamma)$ solution is adjusted to $I4/mcm(00\gamma)$, γ should increase with pressure in the interval: $1.28 < \gamma < 1.36$ [13], therefore passing through the commensurate value of $4/3$ at 72 GPa. This makes the Sc-II phase unique in the sense that it gives one an opportunity to directly perform electronic structure calculations for a complex composite phase.

Generally, the lack of periodicity makes the direct application of first-principle methods to IC structures problematic. Usually, a complex structure is approximated by a periodic analogue and the *ab initio* calculations are performed for that approximant. In principle, one can approximate an IC structure with a very large supercell, whose commensurate ratio approaches the IC one. However, this approach has a few drawbacks: (i) It might not be feasible to calculate a sufficient large periodic structure, and (ii) one is entirely at the mercy of available experimental data when modeling such a structure. Needless to say, such an approach lacks any predictive power. In the case of Sc-II, we have also a question of whether the IC structure becomes commensurate at a certain pressure. In fact, stan-

standard *ab initio* techniques are able to some degree to answer this question. One can approximate the IC structure with a set of commensurate analogues with commensurate ratios about γ . First-principles calculations are able to discriminate the structure with the lowest total energy; thus, already at this stage one can check the experimental prediction. Furthermore, within the framework of the density functional theory (DFT), the total energy is a function of structural parameters and must have a minimum for the set of parameters corresponding to the ground state structure. In the case of 1D IC systems [16], the total energy is a continuous function of the c_1/c_2 ratio and therefore can be expanded about the minimum corresponding to the true IC ratio γ of the complex phase.

In this Letter, we propose a procedure enabling one to obtain the total energy of an IC structure and to determine its structural parameters using *ab initio* techniques for periodic solids. We calculate the dependence of γ on the applied pressure and show that it is qualitatively different from the one predicted from experimental data. Up to about 60 GPa, γ increases with pressure, in agreement with experimental observations, but then it starts decreasing again down to the values comparable to those observed at low pressure, where Sc-II phase is metastable. The decrease of γ with pressure above 60 GPa is accompanied by changes in the band structure that might signify a structural instability of the Sc-II phase.

The calculations were performed in the framework of DFT using the VASP program [17,18], a robust and highly efficient implementation of the projector augmented-wave (PAW) method [19]. To describe the electronic structure of different Sc phases, we used the Sc PAW potential with $3s^2 3p^6 3d^1 4s^2$ valence orbitals, and both the local density approximation (LDA) [20] and the generalized-gradient approximation (GGA) [21,22] of the exchange-correlation functional were applied to treat the electronic exchange and correlation effects. Although both LDA and GGA calculations give qualitatively similar results, GGA agrees quantitatively better with the available experimental data, and in what follows we present the results of our GGA-PW91 calculations. For total energy calculations and relaxation, we used the Methfessel-Paxton smearing method. The structures were relaxed until the Hellman-Feynman forces became less than 10^{-3} eV/Å. The number of k points and plane waves used in the calculations ensured the total energy convergence to be 0.2–0.3 meV/atom.

In order to accurately calculate the dependence of structural parameters of an IC phase on applied pressure, we performed a series of calculations at different volumes within the pressure interval 0–100 GPa by approximating the complex structure with a set of periodic supercells built of n_1 host cells and n_2 guest cells, with commensurate $c_1/c_2 = n_2/n_1$ ratios of about 1.28. The host lattice is bct described by the symmetry group $I4/mcm$ with atoms at

Wyckoff position $8h(x, x + 1/2, 0)$, and the guest lattice is C fct with atoms at $(0, 0, 0)$ and $(1/2, 1/2, 0)$. We chose the following set of values for n_2/n_1 : 6/5, 5/4, 14/11, 4/3, 10/7, and 3/2, which yielded two kinds of structures as far as symmetry was concerned. In the case of even n_2 and odd n_1 the bct cells ($I4/mcm$) were generated, and in the opposite case of odd n_2 and even n_1 simple tetragonal cells, described by space group $P4/mbm$, were built. Then, at each volume, we relaxed all of the analogue structures. We expected that atoms would move away from the superstructure positions in order to mimic the distribution of the IC phase to the degree maximal possible under the constraint of the periodic supercell. Indeed, after the relaxation the host atoms are not described by just one Wyckoff parameter x at different Wyckoff sites [for example, $8h(x, x + 1/2, 0)$ and $16l(x, x + 1/2, z)$ for the 4/3 supercell] but by a set of slightly different Wyckoff parameters $\{x_i\}$ and $\{z_i\}$, corresponding to different atomic sites.

The total energies of the calculated commensurate structures are shown in Fig. 1(a). One can see that in the considered pressure range the 4/3 analogue structure does not appear to be most energetically favorable. Although the structures 14/11 and 4/3 are competing within the pressure interval (40–70 GPa), the energy of the 4/3 analogue lies 2 meV/atom above that of the 14/11 supercell, larger than the accuracy of our calculations. When pressure exceeds 70 GPa, we observe a dramatic increase of the energy difference between the 14/11 and 4/3 analogues. Further, at the highest calculated pressure

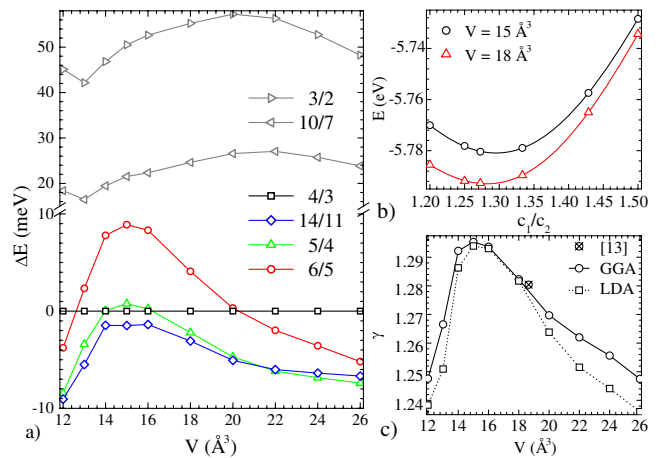


FIG. 1 (color online). (a) Total energies of various commensurate analogues with respect to the energy of the commensurate supercell with $c_1/c_2 = 4/3$ as a function of volume/atom. (b) Total energy as a function of c_1/c_2 (solid line) obtained by a fourth-order polynomial fitting of *ab initio* data (symbols) at the two volumes (energy curve for volume/atom = 15 \AA^3 is shifted down by 0.7 eV). (c) Calculated γ as a function of volume/atom for two different approximations (LDA and GGA) of the exchange-correlation functional. The experimental point is taken from [13].

($V = 12 \text{ \AA}^3$), the energy difference between the 5/4 and 14/11 analogues becomes comparable to the accuracy of the calculations; therefore, these structures become degenerate in energy that might indicate a possibility of a new structural phase transition.

In Fig. 1(b), the dependence of energy on the ratio c_1/c_2 is shown for two chosen volumes. We fitted the calculated values with a fourth-order polynomial, and by finding the minimum of $E = E(c_1/c_2)$ we estimated γ and the corresponding total energy $E = E(\gamma)$ of the IC phase. From the obtained $E = E(V)$ function, the pressure $P(V) = -\partial E(V)/\partial V$ and enthalpy $H(P)$ were calculated. To estimate the internal parameter x of the Wyckoff position $8h$, we first calculated the average value of x for each commensurate analogue at each volume, and then the dependence of \bar{x} on c_1/c_2 was fitted polynomially. Lattice parameters a and c as the functions of pressure were estimated in a similar way (the lattice parameter c of the IC structure is equal to the lattice parameter of the host component c_1). The derived values for lattice parameters, γ , and the Wyckoff parameter of Sc-II at different pressures are summarized in Table I. The calculated dependence $\gamma(V)$ is also given in Fig. 1(c) for two different exchange-correlation functionals. One can see that γ does not pass through the commensurate value 4/3 in the stability region of the Sc-II phase. This discrepancy between experimental and theoretical predictions prompts a more careful reexamination of the x-ray spectrum of Sc-II above 50 GPa.

At this point, we would like to emphasize the importance of structural relaxation, that is, the optimization of the supercell shape and atomic positions, for obtaining accurate and correct structural parameters. The fact that the Sc-II phase is superconducting with a relatively high T_c is an indicator of rather strong electron-phonon coupling. Very recently, it has been suggested that there is no true distinction between a charge density wave (CDW) and a structural phase transition, in particular, an IC lattice transition [23]. It has been shown that the topology of the Fermi surface, which is the characteristic of the metal

TABLE I. Calculated values of pressure, lattice parameters, γ , and Wyckoff parameter for the Sc-II $I4/mcm(00\gamma)$ phase.

$V/\text{atom} (\text{\AA}^3)$	P (GPa)	a (\AA)	c (\AA)	γ	x
12.00	104.64	6.3408	3.1325	1.2476	0.1505
13.00	84.84	6.6355	3.1100	1.2665	0.1511
14.00	67.98	6.9097	3.1037	1.2922	0.1511
15.00	53.82	7.0772	3.1718	1.2953	0.1507
16.00	42.13	7.2124	3.2566	1.2937	0.1504
18.00	25.31	7.4787	3.4000	1.2823	0.1499
20.00	13.83	7.7498	3.6187	1.2697	0.1496
22.00	5.82	7.7988	3.7231	1.2620	0.1493
[13]	23	7.5672	3.4398	1.2804	0.1490
This work	23	7.5235	3.4201	1.2801	0.1498

electronic subsystem, plays a secondary role in the formation of the CDW, and, actually, the strong electron-phonon interaction, which is certainly affected by the electronic structure, is the main driving force of a CDW instability [23]. Therefore, structural relaxation is a key step in the calculations of a complex structure taking into account the interaction between electrons and ions resulting in charge distribution ultimately approaching that of the ground state complex structure.

To see the effect of relaxation, we have built a new set of periodic analogues with the structural parameters given in Table I and calculated their total energies at different volumes without structure optimization. The overall picture obtained in these calculations is similar to that shown in Fig. 1(a), but the energies of analogue structures are shifted upwards with respect to the 4/3 analogue (not shown). Thus, the 4/3 commensurate supercell appears to be energetically most favorable among the unrelaxed structures between 40 and 100 GPa. In Fig. 2(a), the energy of relaxation, defined as the difference between the total energy of the optimized structure and the unrelaxed one, is shown as a function of volume. Notice that the relaxation energies are larger than the total energy differences between competing approximants and they are different for different analogues. Moreover, the 14/11 analogue, appearing as most preferable according to the total energy [Fig. 1(a)], does not have the lowest relaxation energy. This indicates that relaxation energy, though very important, is not totally decisive for the stabilization of the 14/11 analogue. The analysis of the band energy contribution to the total energy, which is essentially a sum over occupied one-electron states, and the remaining terms, the most significant part of which is the electrostatic energy, also shows

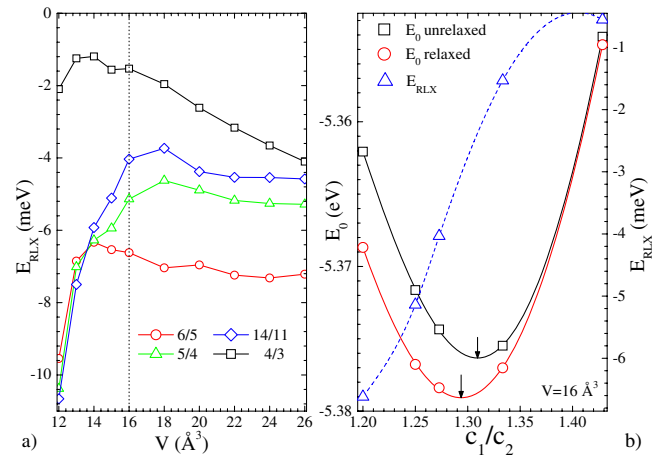


FIG. 2 (color online). (a) Energy of relaxation for a set of competing analogue structures as a function of volume/atom. (b) Total energy E_0 as a function of c_1/c_2 (solid line) obtained by a fourth-order polynomial fitting of *ab initio* data (symbols) for unrelaxed and relaxed supercells (left Y axis) and energy of relaxation E_{RLX} at the volume/atom = 16 \AA^3 (right Y axis). Arrows point to the minimum of the $E(c_1/c_2)$ curves.

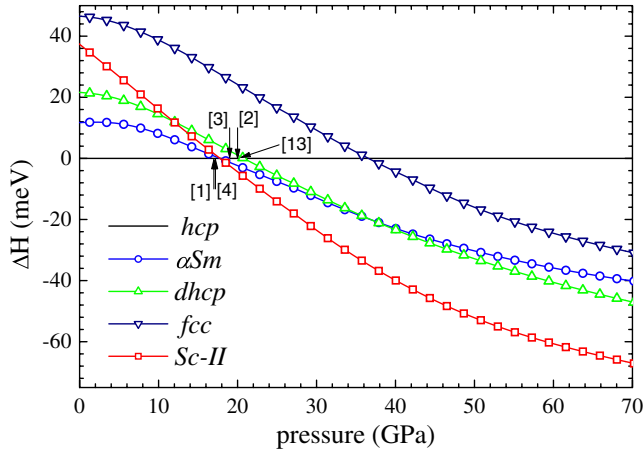


FIG. 3 (color online). Phase diagram of scandium at $T = 0$ K. Arrows point to the onset of transition to the Sc-II phase observed in different experiments. The symbols are just a guide for the eye.

that none of these terms alone can explain the stabilization of the 14/11 structure. Therefore, the 14/11 analogue is favored neither by the ionic charge redistribution during the relaxation nor by the electronic charge redistribution in a relaxed structure alone but by the combination of both terms due to electron-phonon interaction. We stress again that a careful structural relaxation stands out as an absolutely vital procedure enabling us to correctly estimate structural parameters of complex structures. To illustrate this point even further, we show the total energy versus the c_1/c_2 ratio for the unrelaxed and relaxed structures together with the relaxation energy for the chosen volume ($V = 16 \text{ \AA}^3$) [Fig. 2(b)]. The relaxation energy contribution shifts the minimum of the $E(c_1/c_2)$ curve that results in a more accurate determination of γ .

Finally, we have calculated the enthalpy of the Sc-II phase in order to estimate the hcp to Sc-II transition pressure. In Fig. 3, the enthalpies of different Sc phases with respect to that of hcp are shown versus pressure. In addition to the experimentally observed hcp and Sc-II phases, we also considered the αSm , dhcp, and fcc phases. According to our calculations, at $T = 0$ K the transition from hcp to Sc-II phase occurs at 17.8 GPa that is in excellent agreement with low-temperature data by Wittig *et al.* [1]. The transition is accompanied by the volume change of 1.5% that is in very good agreement with the data by McMahon *et al.* [13]. However, the most surprising result is that the enthalpy of the αSm structure is competing with those of hcp and Sc-II at the transition point and, actually, all three phases appear to coexist in the vicinity of 17.8 GPa. It indicates a complex mechanism of the tran-

sition and calls for more theoretical and experimental work to explore its nature.

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*Sergiu.Arapan@fysik.uu.se

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