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Structural, elastic, and high-pressure properties of cubic TiC, TiN, and TiO

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We have studied the structural and elastic properties of TiC, TiN, and TiO by means of accurate first-principles total-energy calculations using the full potential linear muffin-tin orbital method. The calculations are based on the density functional theory and we have used the local-density Hedin-Lundqvist parametrization as well as the generalized gradient approximation proposed by Perdew and Wang for the exchange and correlation potential. The calculated values for the equilibrium volume, bulk modulus, and elastic constants are generally in very good agreement with experiments. At elevated pressures all these compounds are predicted to undergo a structural phase transition from the relatively open NaCl structure into the more dense CsCl atomic arrangement. The predicted transition pressure for TiO can be reached in modern high-pressure laboratories.

I. INTRODUCTION

The transition metal compounds of the type MX, where M denotes a transition metal element and X denotes one of the nonmetallic elements C, N, or O, are generally very hard materials and they often crystallize in the rocksalt structure. These compounds have great scientific and technological interest. The titanium compounds belong to the class of so-called refractory metal compounds. Further, they have high melting points and extreme hardness, properties which are typically found for covalent crystals.[1] It is interesting that properties associated with covalent bonding are found in a set of systems which display a crystal structure normally associated with ionic bonding (NaCl). The type of bonding found for the MX systems is not typically ionic but as shown in Ref. 2 more covalent and the occurrence of an ioniclike structure in combination with covalent like hardness is very interesting. In addition they show metallic conductivities comparable with those of pure transition metals. TiN is presently one of the most important materials for hardness and corrosion resistant coating. Presently interest is also developing within the microelectronic industry for the use of TiN as an electrically conducting barrier.

The local-density approximation (LDA) within the density functional theory (DFT) has been proven to be a very useful approximation for calculating electronic and ground state properties of solids, molecules, and atoms. Although this approach works very well for most systems there are cases, like for example the 3*d* transition metals, where it underestimates the equilibrium volume and overestimates the bulk modulus.[3,4] Moreover it does not give the correct ground state for iron metal.[5] It has been suggested that these drawbacks can be removed by improving upon the LDA exchange-correlation functional with corrections arising from the gradient of the charge density. Perdew and Wang (PW) (Ref. 6) have proposed the so-called generalized gradient approximation (GGA) which hereafter is referred to as PW91.[7] It has been demonstrated that PW91 gives a considerable improvement of the ground state properties of many atomic, molecular, and solid state systems.[8] As an example of this we mention the recent work of Ozolins and Körling[9] who have performed calculations, based on the full potential linear muffin-tin orbital method using PW91, for the structural and cohesive properties of transition metals. They have shown that gradient corrected full potential calculations give a significant improvement over calculations based on the local density approximation (LDA). Further, they have suggested that the full potential treatment is important in combination with the gradient corrected potentials.

In the literature there is unfortunately almost a complete lack of elastic constant calculations using the GGA and it is hard to conclude whether or not the GGA reproduce this quantity better than LDA. Our own recent calculations of the Fermi surface (FS) for the noble metals,[10] using a full potential linear muffin-tin orbital method (FPLMTO) calculation within the LDA, gave improvement over LMTO-ASA (atomic sphere approximation) calculations and gradient corrected FPLMTO calculations further improve the agreement with experiments. One of the purposes of the present paper is to continue to investigate to what extent gradient-corrected FPLMTO calculations improve the results for the structural and elastic properties of solid state systems.

The study of the electronic structure of these technologically interesting materials is an important step when trying to develop an understanding of their basic properties. Neckel *et al.*[11] have performed self-consistent band structure calculations for the carbides, nitrides, and oxides of titanium, vanadium, and scandium using the augmented-plane-wave method together with the Xα method for exchange. Zhukov *et al.*[12] have calculated the energy-band structure and chemical bonding in titanium and vanadium carbides, nitrides and oxides using the linear muffin-tin orbitals (LMTO) method within the atomic sphere approximation (ASA). They have determined the equilibrium lattice constants, bulk moduli, cohesive energies and energies of vacancy formation for these materials. They overestimated the equilibrium volumes for TiN and TiO and their calculated values of the bulk moduli for TiC and TiN are very large in comparison to the experimental values. Price *et al.*[13] have studied the electronic structure, total energies, equilibrium lattice constant, bulk moduli and fracture properties of stoichiometric TiC using the full potential linear muffin-tin orbitals (LMTO) method with the LDA approximation for the exchange-correlation potential. Häglund *et al.*[14] have studied the bonding properties of transition metal carbides and nitrides. They have concluded that the *ab initio* results on enthalpies of formation and cohesive energies are adequate for the analysis of the trends in bonding energies. Their calculations show good agreement with experimental data. On the experimental side there are also a lot of recent efforts to study the hardness and elastic properties of TiN using different techniques such as Brillouin scattering and depth-sensing indentation,[15] as well as by continuous indentation technique[16] and by line-focus acoustic microscopy.[17]

The rest of the paper is organized as follows. In Sec. II we describe the details of the calculations and in Sec. III we discuss our results for the electronic structure, lattice stability and elastic constants and high pressure structural phase stability. Finally Sec. IV contains some concluding remarks.

II. DETAILS OF CALCULATIONS

In our present calculations we use the full-potential linear muffin-tin-orbital (FPLMTO) method.[18] The calculations are based on the density functional approximation and we use the Hedin-Lundqvist (HL) (Ref. 19) parametrization and the GGA (Refs. 7 and 20) for the exchange and correlation potential (XC). Basis functions, electron densities, and potentials were calculated without any geometrical approximation. These quantities were expanded in combinations of spherical harmonic functions (with a cutoff $\ell_{\max}=8$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region. The muffin-tin spheres occupied approximately 50% of the unit cell. The radial basis functions within the muffin-tin spheres are linear combinations of radial wave functions and their energy derivatives, computed at energies appropriate to their site and principal as well as orbital atomic quantum numbers, whereas outside the muffin-tin spheres the basis functions are combinations of Neuman or Hankel functions.[21,22] In the calculations reported here, we made use of pseudocore *p* states of Ti and valence band *s,p,* and *d* basis functions with corresponding two sets of energy parameters, one appropriate for the semicore *p* states, and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well converged basis. For sampling the irreducible wedge of the Brillouin-zone we used the special k-point method.[23] In addition, in order to speed up the convergence of the **k**-point sampling, we have associated each calculated eigenvalue with a Gaussian function having a width of 20 mRy.

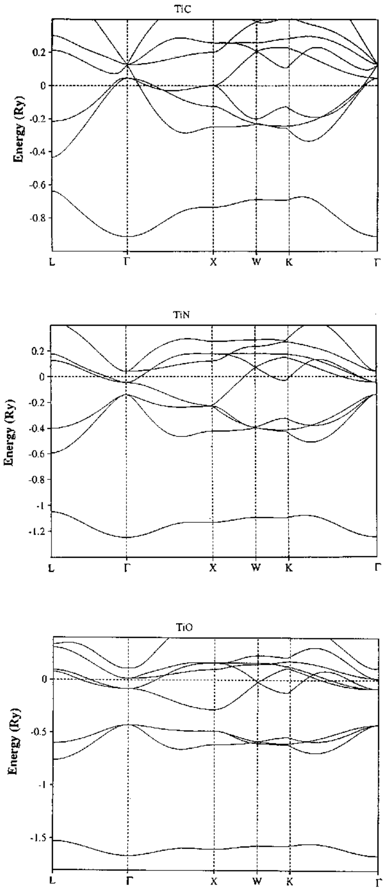

FIG. 1. Energy band structure of TiC, TiN, and TiO along the major symmetry directions. The Fermi level (E_F) is set to be at zero energy.

For a cubic material there are three independent elastic constants; C_{11}, C_{12}, and C_{44}. Resistance to shear distortions of a cubic crystal is best characterized by the two moduli $C'=(C_{11}\text{-}C_{12})/2$ and C_{44}. The shear constant C_{44} is related to an orthorhombic deformation whereas C' is related to a tetragonal deformation. We evaluated C' and C_{44} by calculating the total energy for a few strains of the systems, as described in for instance Ref. 20. In the calculation of structural stabilities we evaluated the free energy, $F=E+PV$, and compared this property for the different structures.

III. RESULTS AND DISCUSSION

A. Electronic structure

In Fig. 1 we show our calculated energy band structure within LDA for TiC, TiN, and TiO. The calculated band structure within GGA is very similar to the LDA results, so we show only the LDA band structure. The band structures of these three different materials are closely related to each other. They are all characterized by an energetically low-lying band, which is derived from the 2*s* states of the nonmetal. At a somewhat smaller binding energy three overlapping bands are found and these bands originate from the state at Γ. These bands are mainly composed of the 2*p* states of the nonmetal atom but contain also a significant contribution of states with *d* symmetry. The next five bands are predominantly derived from transition-metal *d* states, but exhibit also

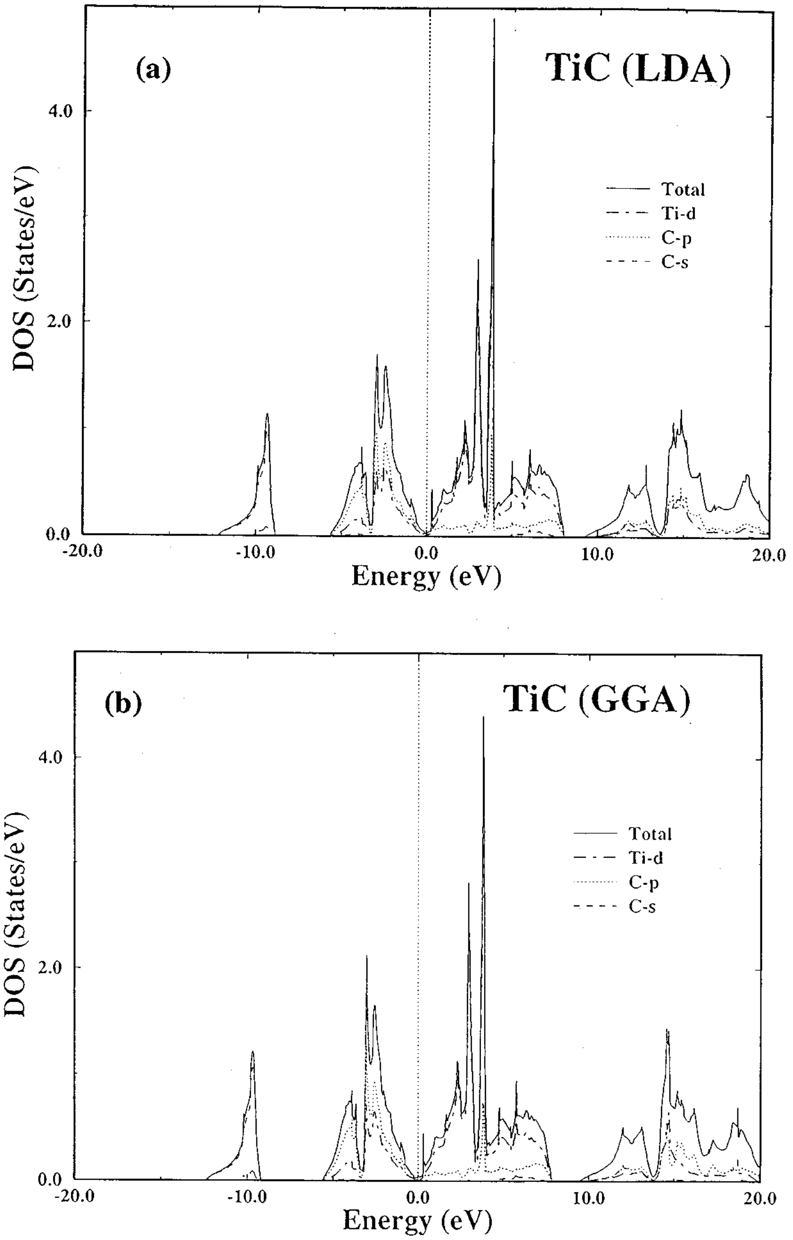

FIG. 2. Calculated density of states (DOS) for TiC (a) LDA and (b) GGA. The full line shows the total DOS, while the long dashed, dotted, and dashed lines show the Ti 3*d*-partial, C 2*p*-partial, and C 2*s*-partial DOS, respectively. The Fermi level is set at zero energy and marked by a vertical dotted line.

some *p* character. The highest-lying bands represent a mixture of states with different symmetries, derived from both the M and X constituents.

In Fig. 2, we show the density of states (DOS) for TiC as obtained by means of the LDA and GGA approximations. Note that the calculated DOS is very similar for the two cases, except for that in GGA the carbon *s* state lies a little bit lower in energy. In TiC one might expect very strong bonding because the Fermi energy (E_F) intersects the pronounced pseudogap where the DOS at E_F is very low. The states below E_F are dominated by strongly hybridized bonding combinations of Ti 3*d* orbitals of e_g symmetry and C *p*-derived orbitals, with some contribution from Ti-Ti t_{2g} σ and C *p*-Ti t_{2g} π bonding orbitals. Both the Ti e_g-C *p* antibonding states and most of the Ti t_{2g} derived states are found in the region above the pseudogap, although the latter provide by far the largest contribution to the DOS in this energy region.

The density of states (using LDA) for TiN is shown in Fig. 3. The calculated DOS is very similar to that for TiC except that the nitrogen *s* and *p* states are situated at a lower energy than the corresponding carbon states. Therefore the DOS shows a low lying structure, well separated from the features between 0 and 8 eV, which is due to N 2*s* states. Also, the N 2*p* and Ti 3*d* states are further apart in energy compared to TiC, resulting in weaker *p*-*d* mixing. The states between 0 and 8 eV below E_F are mainly composed of hybridized Ti 3*d* and N 2*p* states. In contrast to the case for TiC, E_F lies on a sharply increasing peak which is mainly made up from Ti 3*d* states. Thus the metallic properties are dominated by states originating from the transition metal atoms.

The change in the electronic structure when going from TiC to TiN is further accentuated when considering TiO (Fig. 4, LDA calculation). Thus in TiO, the O 2*s* states lie very far below E_F in comparison to the C 2*s* and the N 2*s* states in

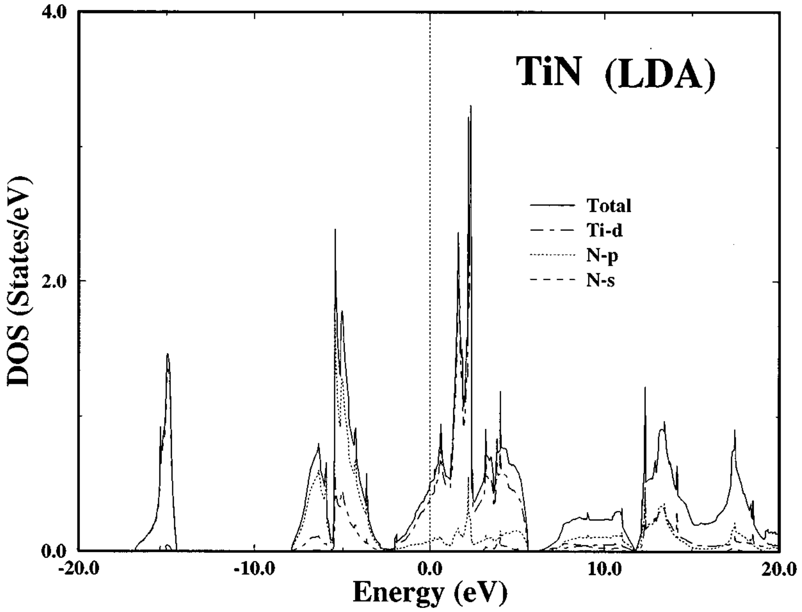

FIG. 3. Calculated density of states (DOS) for TiN (LDA) . The full line shows the total DOS, while the long dashed, dotted, and dashed lines show the Ti 3*d*-partial, N 2*p*-partial, and N 2*s*-partial DOS, respectively. The Fermi level is set at zero energy and marked by a vertical dotted line.

TiC and TiN, respectively. As shown in Fig. 4, these O 2*s* states are situated around 22 eV below E_F and they are separated by about 11 eV from the bonding Ti 3*d* and O 2*p* states. The *d*-*p* energy difference is also larger so that there is now a real gap of about 2 eV which separates the antibonding (mainly Ti 3*d*) and (mainly O 2*p*) bonding states. In comparison to TiC and TiN the states at the Fermi level for TiO are more separated from the bonding and antibonding states. Therefore the occupied part of the states close to the Fermi level contain more *d* electrons in TiO than in TiN. Thus the occupied conduction electron states are in TiO heavily dominated by 3*d* electrons.

B. Lattice stability and elastic constants

In Table I and Figs. 5 and 6, we give our calculated values for the equilibrium volume and bulk modulus for TiC, TiN, and TiO together with the experimental values.[24] Our LDA results for the equilibrium volumes for TiC and TiN are within 5% of the experimental volume. This type of error for the equilibrium volume is expected in the LDA. When we use GGA for the exchange-correlation potential the calculated data are within less than 1% of the experimental volumes for TiC and TiN. The case of TiO is different since already LDA gives a very good volume, i.e., within 1% of the experimental value, while GGA overestimates the volume by 6.3%. If we compare our calculated LDA values for TiC with the calculations of Zhukov *et al.*[12] and Price *et al.*,[13] we find that their equilibrium volumes are within 4% of the experimental volume which is in complete agreement with our LDA results. For TiN and TiO, Zhukov *et al.*[12] found that their calculated equilibrium volumes are 6% and 30% larger than the experimental volumes, respectively.

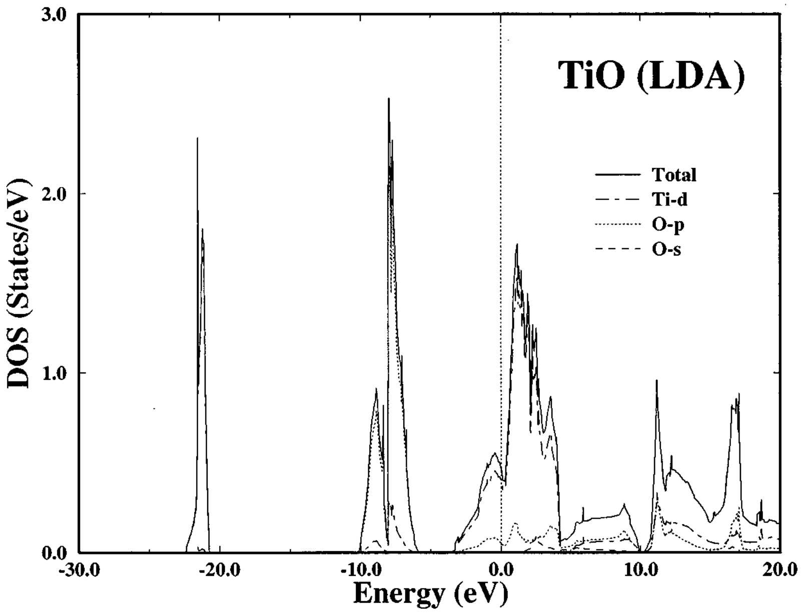

FIG. 4. Calculated density of states (DOS) for TiO (LDA). The full line shows the total DOS, while the long dashed, dotted, and dashed lines show the Ti 3*d*-partial, O 2*p*-partial, and O 2*s*-partial DOS, respectively. The Fermi level is set at zero energy and marked by a vertical dotted line.

TABLE I. Calculated and experimental volume (Å^3) and bulk modulus (Mbar).

	Volume	Bulk modulus	LDA			GGA		
	($V^{\text{expt.}}$)	($B^{\text{expt.}}$)	$V^{\text{theo}}/V^{\text{expt.}}$	$B^{\text{theo}}_{V\ \text{theo}}$	$B^{\text{theo}}_{V\ \text{expt.}}$	$V^{\text{theo}}/V^{\text{expt.}}$	$B^{\text{theo}}_{V\ \text{theo}}$	$B^{\text{theo}}_{V\ \text{expt.}}$
TiC	10.06	2.4	0.956	2.7	2.3	0.998	2.2	2.1
TiN	9.53	3.2	0.945	3.1	2.5	0.993	2.7	2.6
TiO	9.14	2.7	0.99	2.8	2.8	1.063	2.3	2.9

Zhukov *et al.*[12] have argued that their overestimation of the volumes is due to the use of the atomic sphere approximation (ASA) which is not suitable for the open NaCl structure. For TiO, they therefore filled the space with additional empty spheres which makes the calculations more closed packed and this reduced the overestimation in volume from 30% to 6%.

The present GGA results for TiO are most interesting. Experimentally it is well established that this compound contains a number of vacancies both on the anion sites as well as on the cations sites.[25] Therefore perfectly ordered TiO has never been prepared. In view of the present very good GGA results for TiC and TiN we have no reason to expect that TiO would be different in this respect. Therefore we claim that our theoretical GGA data are appropriate for perfectly ordered TiO. This suggests that we have reached a level of accuracy where we can use theoretical calculations for establishing the true behavior of perfectly ordered materials, never realized in nature. Thus based on our present GGA calculations, we predict that the perfectly ordered TiO compound will have a lattice constant of 4.268 Å.

The calculated values of the bulk modulus for TiC are 2.7 and 2.2 Mbar within the LDA and GGA approximations, respectively, while the experimental value is 2.4 Mbar.[26] Thus in the case of TiC LDA overestimates the bulk modulus and GGA underestimates it. The LDA calculated values of Zhukov *et al.*[12] and Price *et al.*[13] are 3.9 and 3.1 Mbar, respectively, which are larger than our calculated values and experiments. For TiN our LDA calculated value for the bulk modulus is in very good agreement with the experimental value[17] but is somewhat less good in the GGA. Zhukov *et al.*[12] calculated a bulk modulus of about 3.9 Mbar, which again is very high in comparison to experiments. The LDA calculated value for TiO is in very good agreement with experimental data[27] while it is somewhat less close to experiments for the GGA results. Zhukov *et al.*[12] have calculated the bulk modulus for TiO and their value is 3.56 Mbar without empty spheres and 1.76 Mbar with empty spheres. The experimental value of 2.8 Mbar is in between these two values.

Our calculated results for the elastic constants are compiled in Table II and Fig. 7. For TiC we see that the theoretical values of C_{11} and C_{44} in LDA are larger than the experimental values,[28] while the calculated value for C_{12} agrees with the experimental data. When we use GGA, the theoretical values of C_{11}, C_{12}, and C_{44} are found to be lower than the experimental numbers but are nevertheless in very good agreement with the experimental data. For TiN, within LDA, our calculated data of C_{11} and C_{44} are higher than the experimental values[17] but GGA reduces the values of C_{11} and C_{44} and gives very good agreement with experiment. The calculated value for C_{12} is lower than the experimental value, both in LDA and GGA. For TiO, there exist no ex-

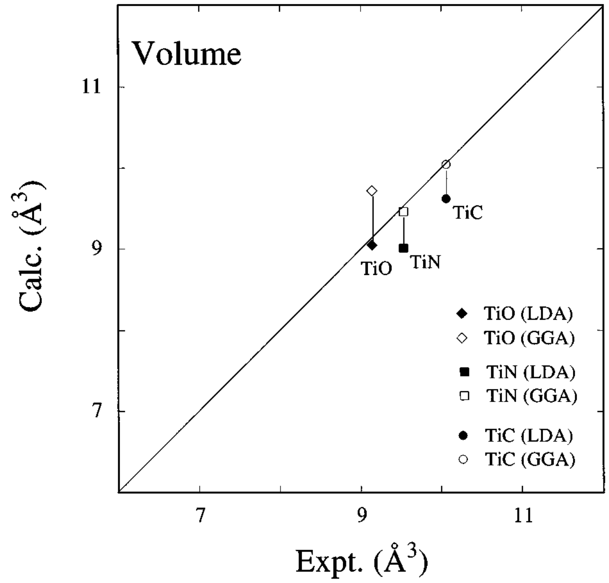

FIG. 5. Calculated and experimental volumes for TiC, TiN, and TiO both in LDA and GGA.

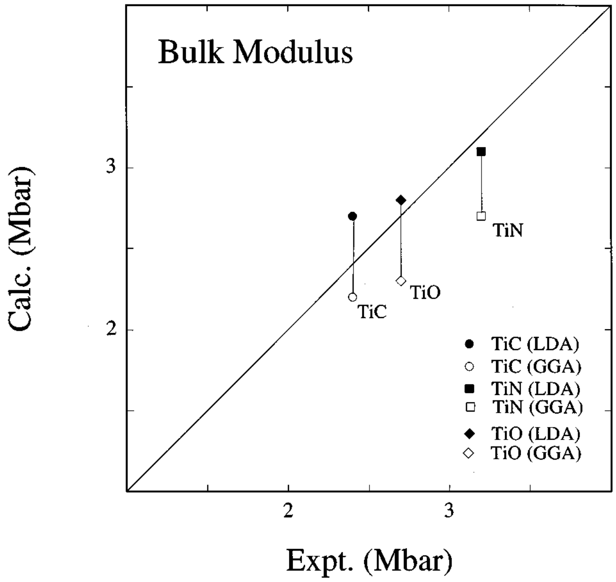

FIG. 6. Calculated and experimental bulk modulus for TiC, TiN, and TiO both in LDA and GGA. The calculated bulk modulus was obtained at the theoretical equilibrium volume.

TABLE II. Calculated and experimental elastic constants (Mbar).

	C_{11}			C_{12}			C_{44}		
		Theory			Theory			Theory	
	Expt.	LDA	GGA	Expt.	LDA	GGA	Expt.	LDA	GGA
TiC	5.13	6.06	4.7	1.06	1.06	0.97	1.78	2.3	1.67
TiN	6.25	7.35	6.10	1.65	0.93	1.00	1.63	2.5	1.68
TiO		6.93			0.73			1.3	

perimental data and we hope our present work will stimulate some more work on this material.

For the present type of materials it seems that we have now reached a point where theory is close to replace experiments as regards certain bulk material properties. This is especially so for the lattice constant. In view of the experimental difficulties to determine the bulk modulus, one could perhaps also argue that presently the theoretical values are equally reliable as the experimentally determined values. As regards the elastic constants, theory seems again capable to produce data which are almost of experimental quality. In this respect theoretical calculations can be of great help in establishing the limiting idealized behavior in the search for improving materials properties. In the present case of superhard NaCl transition metal compound materials, our calculations demonstrate that electronic structure studies now have reached a point where they can usefully complement experimental work in this area and perhaps in certain cases even replace such studies.

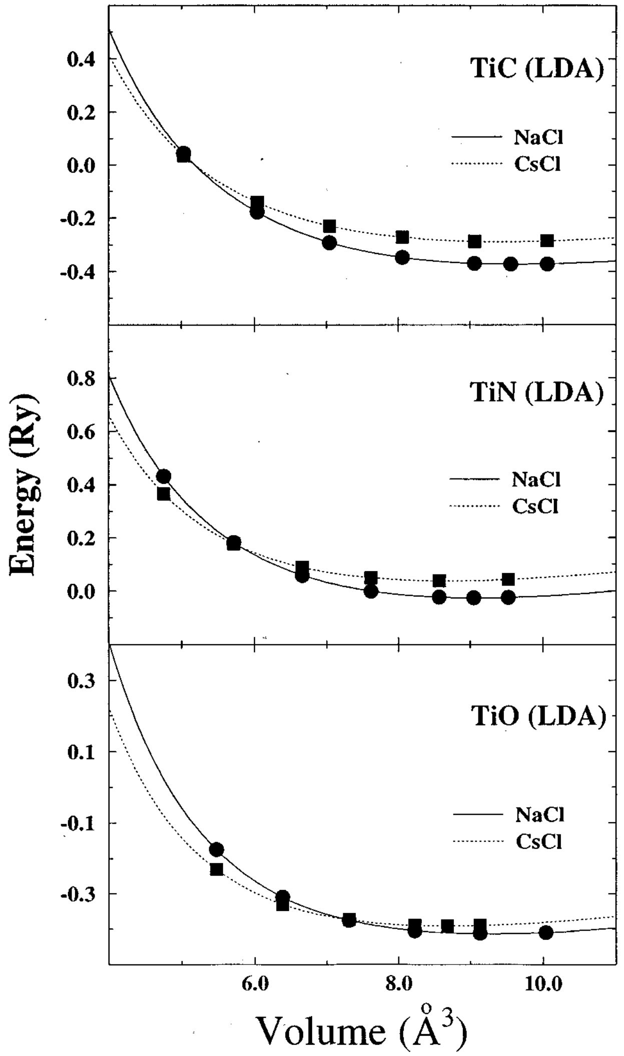

FIG. 8. The total energy as a function of volume for the NaCl and CsCl structures of TiC, TiN, and TiO.

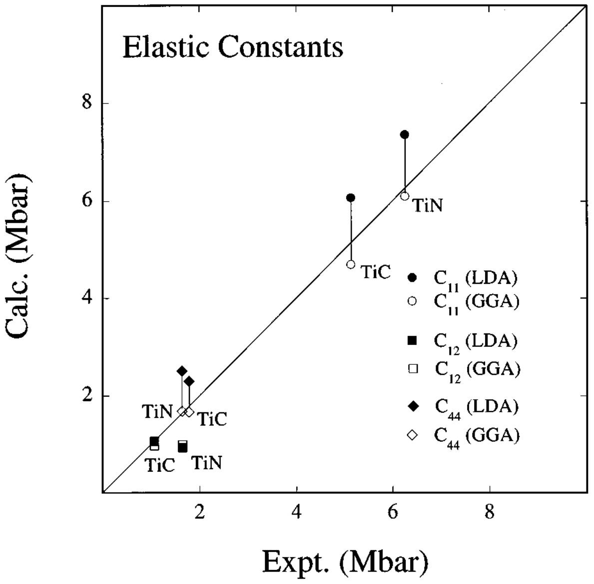

FIG. 7. Calculated and experimental elastic constants for TiC, TiN, and TiO both in LDA and GGA. The calculated elastic constants were obtained at the theoretical equilibrium volume.

C. Structural phase stability at high pressures

Since the superhard materials are used at extreme conditions it seems obvious that it is of interest to study their behavior under very high compressions. Here we would like to study the possibility of structural phase transitions at high-pressures. Such crystallographic transformations could severely limit the usefulness of the present materials under certain extreme conditions. In order to study the structural phase stability for the compounds, the total energies were calculated for both the NaCl and CsCl structures as a function of volume. The behavior of the total energy with volume is given in Fig. 8 for all three compounds. The calculated total energies are fitted to the Murnaghan equation of state,[29] to obtain the pressure-volume relation (shown in Fig. 9). As can been seen from Fig. 8 the NaCl structure is stable at the experimental volume, as it should be, for all three compounds. Under compression, the calculations show that TiC, TiN, and TiO will undergo a structural phase transition from NaCl to CsCl structure. The transition volume for this NaCl → CsCl transition decreases as we go from TiC → TiN → TiO. The calculated transition pressures are 4.9 Mbar, 3.7 Mbar, and 0.8 Mbar for TiC, TiN, and TiO, respectively (compare Fig. 9). From Fig. 9 it is clear that for a given pressure the NaCl structure has a larger volume compared to the CsCl structure. This fact holds for all three compounds and is consistent with the better packing ratio of the CsCl structure. Also, due to the extreme hardness of these materi-

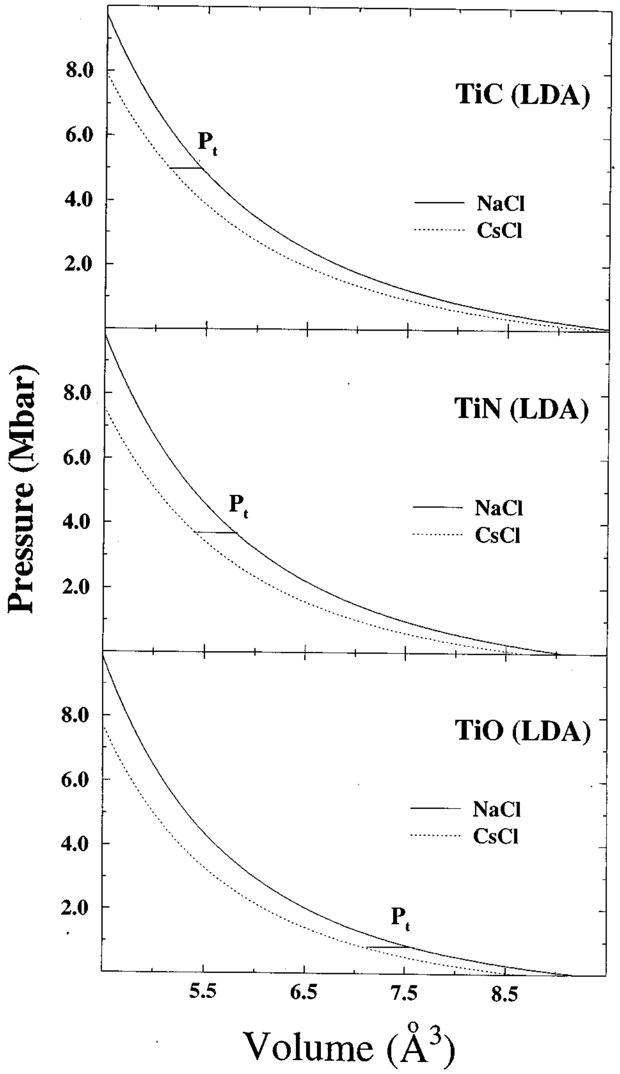

FIG. 9. Calculated electronic pressure as a function of volume for the NaCl and CsCl structures of TiC, TiN, and TiO. P_t is the theoretical calculated transition pressure.

als a pressure of ≈ 10 Mbar is reached already for a compression, $V/V_0 \approx 0.50$, where V_0 is the experimental equilibrium volume. Thus only a relatively small volume compression is needed to induce the CsCl structure. However, due to the incompressibility of these systems the necessary transition pressures are still in the megabar range. We are not aware of any measurements for these materials at extreme pressures. The recent development of the high pressure technique using diamond-anvil cell has made it possible that these pressures are within reach of experiment. We hope that in the near future there will be more high pressure measurements on these technologically important materials. For standard technical applications our calculated transition pressures are all sufficiently high not to cause any problems for the functional behavior of the present NaCl compounds.

IV. CONCLUSIONS

To conclude, we have studied the electronic structure, elastic properties, and lattice stability of TiC, TiN, and TiO. Our calculations show that stoichiometric TiN is less compressible than TiC in agreement with the experimental data. Within LDA, our calculations show a fair agreement with the experimental data. When the calculations are performed in GGA, our results show a substantial improvement over LDA. We are neither aware of any published data for the elastic constants of TiO nor of any high pressure studies on these materials so our calculations can be used to cover this lack of data for this fundamentally important material.

The present results demonstrate that when the most developed theoretical electronic structure calculations are performed one can actually reach a level of accuracy for certain fundamental materials properties where theory can replace experiment. This means, at least for some materials properties and classes of systems, that we have now arrived at a stage where the search for new materials can be performed by computers and that thereby no lack of accuracy is lost. Clear limitations of this approach remain of course for instance in cases when the materials performance is heavily connected to the behavior of vacancies or to deficiencies in the stoichiometry of the physical systems.

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[1] L.E. Toth, *Transition Metal Carbides and Nitrides* (Academic, New York, 1971).

[2] D.L. Price and B.R. Cooper, Phys. Rev. B **39**, 4945 (1989).

[3] V.L. Moruzzi, J.F. Janak, and A.R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[4] A.T. Paxton, M. Methfessel, and H.M. Polatoglou, Phys. Rev. B **41**, 8127 (1990).

[5] C.S. Wang, B.M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[6] J.P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986); J.P. Perdew, *ibid.* **33**, 8822 (1986); **34**, 7406 (1986).

[7] J.P. Perdew, in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Academie Verlag, Berlin, 1991), p. 11.

[8] 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).

[9] V. Ozolins and M. Körling, Phys. Rev. B **48**, 18 304 (1993), and references cited therein.

[10] R. Ahuja, S. Auluck, P. Söderlind, O. Eriksson, J.M. Wills, and B. Johansson, Phys. Rev. B **50**, 11 183 (1994).

[11] A. Neckel, P. Rastl, R. Eibler, P. Weinberger, and K. Schwarz, J. Phys. C **9**, 579 (1975).

[12] V.P. Zhukov, V.A. Gubanov, O. Jepsen, N.E. Christensen, and O.K. Andersen, J. Phys. Chem. Solids **49**, 841 (1988).

[13] D.L. Price and B.R. Cooper, Phys. Rev. B **39**, 4945 (1989); D.L. Price, B.R. Cooper, and J.M. Wills, *ibid.* **46**, 11 368 (1992).

[14] J. Häglund, A.F. Guillermet, G. Grimvall, and M. Körling, Phys. Rev. B **48**, 11 685 (1993).

[15] X. Jiang, M. Wang, K. Schmidt, E. Dunlop, J. Haupt, and W. Gissler, J. Appl. Phys. **69**, 3053 (1991).

[16] D.S. Stone, K.B. Yoder, and W.D. Sproul, J. Vac. Sci. Technol. **A9**, 2543 (1991).

[17] J.O. Kim, J.D. Achenbach, P.B. Mirkarimi, M. Shinn, and S.A. Barnett, J. Appl. Phys. **72**, 1805 (1992).

[18] J.M. Wills (unpublished); J.M. Wills and B.R. Cooper, Phys. Rev. B **36**, 3809 (1987).

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

[20] P. Söderlind, Ph.D. thesis, Uppsala University, 1994.

[21] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[22] H.L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).

[23] D.J. Chadi and M.L. Cohen, Phys. Rev. B **8**, 5747 (1973); S. Froyen, *ibid.* **39**, 3168 (1989).

[24] R.W.G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963), Vol. 1, p. 90.

[25] N.J. Doyle, J.K. Hulm, C.K. Jones, R.C. Miller, and A. Taylor, Phys. Lett. **26A**, 604 (1968).

[26] R. Chang and L.J. Graham, J. Appl. Phys. **37**, 3778 (1966).

[27] M.D. Banus and M.C. Lavine, High Temp. High Press. **2**, 671 (1970).

[28] M.M. Choy, W.R. Cook, R.F.S. Hearmon, H. Jaffe, J. Jerphagnon, S.K. Kurtz, S.T. Liu, and D.F. Nelson, in *Elastic, Piezoelectric, Pryoelectric, Piezooptic, Electrooptic Constants and Nonlinear Dielectric Susceptibilities of Crystals*, edited by K.-H. Hellwege and A.M. Hellwege, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol. 11 (Springer, Berlin, 1979).

[29] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA **30**, 244 (1944).