PHYSICAL REVIEW B VOLUME 60, NUMBER 22 1 DECEMBER 1999-II

# Theoretical studies of substitutional impurities in molybdenum carbide

Håkan W. Hugosson
*Condensed Matter Theory Group, Department of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden and Inorganic Chemistry Group, Ångström Laboratory, Box 538, S-751 21 Uppsala, Sweden*

Lars Nordström
*Condensed Matter Theory Group, Department of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden*

Ulf Jansson
*Inorganic Chemistry Group, Ångström Laboratory, Box 538, S-751 21 Uppsala, Sweden*

Börje Johansson and Olle Eriksson
*Condensed Matter Theory Group, Department of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden*

(Received 27 May 1999)

First-principles full-potential linear muffin-tin orbital calculations have been used to study the effect on the cohesion and electronic structure of cubic $\delta$-MoC when 25% of the carbon is substituted for boron, nitrogen, or oxygen and when 25% of the molybdenum is substituted for niobium, tungsten, or ruthenium. A thorough study of the changes in the electronic structure and the effect of these on the properties of the compounds is made. Special attention is paid to the character (ionic, covalent, or metallic) of the states becoming occupied (or unoccupied) due to the substitution. A study is also made on the properties of the quaternary alloy $Mo_{0.75}W_{0.25}C_{0.75}N_{0.25}$. This substitution is shown to harden $\delta$-MoC. [S0163-1829(99)02646-6]

## I. INTRODUCTION

Today, a large number of transition-metal carbide phases are known. However, thermodynamically stable binary carbides are only formed by the transition metals in groups IV, V, and VI and by Mn in group VII. From a structural point of view, most of these carbides (except chromium carbides) can be described as a stacking of close-packed metal layers with carbon interstitial sites between the metal planes. The transition-metal carbides have a unique combination of properties, e.g., high hardness, high melting point, and excellent electrical conductivity, making them suitable as bulk or thin film materials in many technological applications. Moreover, some group-VI transition-metal carbides, like MoC, have a high catalytic activity being comparable to Pt.[1] In order to make technological use of this catalytic property MoC is deposited as thin films. Many studies have shown that the cubic $\delta$-MoC phase (NaCl structure) usually is formed during thin-film deposition.[2] It is therefore important to study the $\delta$-MoC phase, a high-temperature phase, in more detail. Stoichiometric binary refractory compounds have been studied in detail and have found wide application. It has been found that substituting the nonmetal sublattice of binary compounds with atoms of another kind often makes it possible to increase the hardness and elastic moduli. Since this alloying leads to noticeable changes in the electro- and thermophysical, magnetic and superconducting parameters,[3] it is important to also study the ternary compounds with respect to stability. It is especially interesting to investigate the chemical bonding and structural properties of the transition-metal carbides in a widened perspective, and to make a comparison of phase stability and other cohesive properties of the carbides, borides, nitrides, and oxides. Admittingly, some of the studied compounds are somewhat hypothetical since they have yet to be synthesized. However, we chose to study them in order to obtain a broader understanding of the chemical bonding in these systems.

Given the technological interest in transition-metal compounds and the large experimental activity, many theoretical calculations have been made on these systems using a wide variety of techniques. Earlier work in this field is summarized in two review articles by Calais[4] and Neckel.[5] The reviews by Johansson[6] and Schwarz[7] are other good starting points in the field. Theoretical studies of substitutional impurities in transition-metal carbides are reviewed by Ivanovskii and Shveikin which include some studies of $3d$ and $4d$ metal impurities in $\delta$-MoC.[8] Ivanovskii and co-workers[3,9] have also done work on metal and nonmetal substitutional impurities in TiC using a linear muffin-tin orbital (LMTO)-Green's function method and we have ourselves presented studies of phase stability and bonding in stoichiometric and substoichiometric MoC.[10] A recent study of $TiC_xN_x$ has been made by Jhi and Ihm using pseudopotential methods.[11] Until now, to the best of our knowledge, there has been no work studying a range of both metal and nonmetal substitutional impurities in MoC. Furthermore, to our knowledge no other work on substitutional impurities in transition metal carbides has been made using accurate all electron, full-potential methods. The aim of the present investigation is to study trends in cohesive energy, electronic structure, and bulk modulus when introducing metal and nonmetal substitutional impurities in $\delta$-MoC.

The $\delta$-MoC phase is the analog of the well-known NaCl structure with a fcc Bravais lattice and Mo at (0,0,0) and C at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. When studying the $\delta$-MoC phase with 25% substitutional impurities a supercell consisting of 4Mo and 4C was

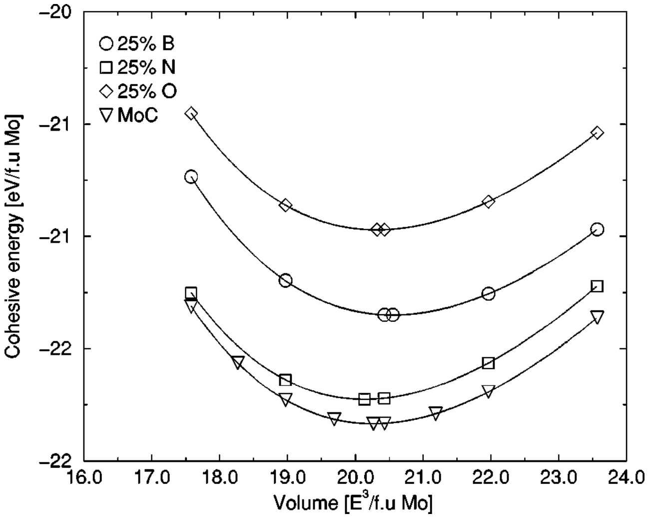

FIG. 1. Generalized cohesive energy for 25% substitutional impurities, $MoC_{0.75}B_{0.25}$, MoC, $MoC_{0.75}N_{0.25}$, and $MoC_{0.75}O_{0.25}$.

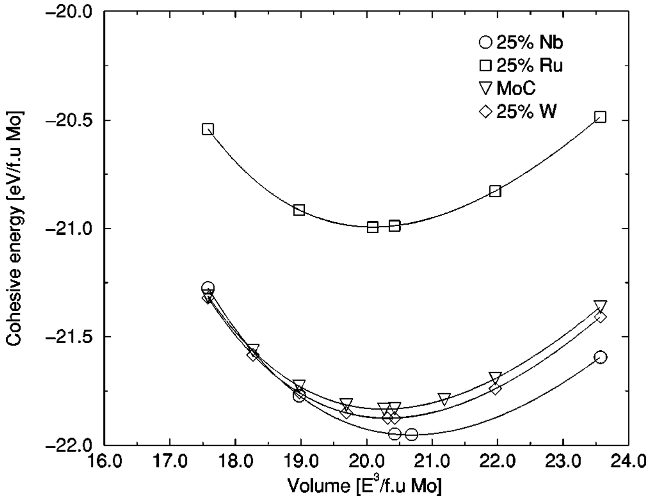

FIG. 2. Generalized cohesive energy for 25% substitutional impurities, $Mo_{0.75}Nb_{0.25}C$, $Mo_{0.75}Ru_{0.25}C$, MoC, and $Mo_{0.75}W_{0.25}C$.

created; one of the carbon atoms was then replaced with either a B, N, or O atom creating $Mo_4C_3B$, $Mo_4C_3N$, and $Mo_4C_3O$, respectively. Similarly, one of the Mo atoms in the supercell was replaced by Nb, Ru, or W when studying metal substitutions. Due to the presence of the substitutional impurity the symmetry of the structure is changed and there are now two inequivalent types of Mo atoms or C atoms, respectively: one which has a substitutional impurity as its nearest neighbor and one that does not. The choice of nonmetal substitution for B, N, and O comes naturally, while the choice of Nb, W, and Ru is made to illustrate the effect of substitution with an atom species with one less valence electron (Nb) and an atom with the same number of valence electrons (W). The choice of Ru which has two more valence electrons than Mo is made since substitution with Tc (one more valence electron) is unlikely to be realized in experiment.

## II. METHOD

The calculations presented here have been made using a full-potential linear muffin-tin orbital method (FP-LMTO) within the local density approximation (LDA) of density functional theory (DFT).[12,13] The function used for the exchange correlation has been the Hedin-Lundqvist scheme. In the FP-LMTO method the unit cell is divided into nonoverlapping muffin-tin spheres, inside of which the basis functions were expanded in spherical harmonics up to a cutoff in angular momentum, $l_{max}=6$. The basis functions in the interstitial region, outside the muffin-tin spheres, are Neumann or Hankel functions. To speed up the convergence each eigenvalue was convoluted with a Gaussian of a width of 20 mRy. Energy convergence in terms of the number of **k** points has also been reached so that this has a minimal effect when comparing energies of different compounds. When describing the atoms of the crystal the electrons are divided into core, pseudocore, and valence states. For the Mo atom the $5s$ and $4d$ were treated as full valence electrons while the $4p$ and $4s$ were treated as pseudocore. The pseudocore and valence states were allowed to hybridize in one common energy panel. All the structures were relaxed in the lattice parameter $a$. This setup does not allow for local relaxations around the impurity atoms; such a relaxation would likely lower the equilibrum energies somewhat[14] but would require a larger supercell. The total energy vs volume curves were subsequently fitted to a Murnaghan equation of state to find theoretical ground-state energies, $E_{eq}$, and equilibrium volumes, $V_{eq}$. The bulk moduli have likewise been obtained from the Murnaghan equation.

## III. COHESIVE ENERGIES AND PHASE STABILITIES

To illustrate the influence of the substitutional impurities on the phase stability of the compounds we display the generalized cohesive energy as a function of volume for 25% substitutional nonmetal impurities in Fig. 1 and for 25% substitutional metal impurities in Fig. 2. The generalized cohesive energy is defined by

$$E^{*}_{coh}=E_{solid}(AB)-E_{atom}(A)-E_{atom}(B). \tag{1}$$

Here, we have consistently used the total energy of the spin degenerate atom from LDA calculations, subtracting this from our equilibrium energy of the compound. The calculated generalized cohesive energies and equilibrium volumes are extracted from these plots and tabulated in Table I.

When carbon is substituted by boron, nitrogen, or oxygen the cohesive energy is decreased. The largest reduction in cohesive energy is for oxygen followed by boron and the smallest reduction is obtained from the substitution with ni-

TABLE I. Equilibrium volumes, $V_{eq}$, and generalized cohesive energies, $E_{coh}$, for 25% substitutional impurities in MoC.

| Phase | $V_{eq}$ (Å$^3$/f.u. Mo) | $E_{coh}$ (eV/f.u. Mo) |
|---|---|---|
| MoC | 20.261 | 21.834 |
| $MoC_{0.75}B_{0.25}$ | 20.553 | 21.350 |
| $MoC_{0.75}N_{0.25}$ | 20.136 | 21.725 |
| $MoC_{0.75}O_{0.25}$ | 20.314 | 20.971 |
| $Mo_{0.75}Nb_{0.25}C$ | 20.681 | 21.953 |
| $Mo_{0.75}Ru_{0.25}C$ | 20.094 | 20.994 |
| $Mo_{0.75}W_{0.25}C$ | 20.316 | 21.875 |

TABLE II. Bulk moduli for 25% substitutional impurities in MoC.

| Phase | Bulk modulus (GPa) |
|---|---|
| MoC | 364 |
| $MoC_{0.75}B_{0.25}$ | 347 |
| $MoC_{0.75}N_{0.25}$ | 370 |
| $MoC_{0.75}O_{0.25}$ | 346 |
| $Mo_{0.75}Nb_{0.25}C$ | 353 |
| $Mo_{0.75}Ru_{0.25}C$ | 359 |
| $Mo_{0.75}W_{0.25}C$ | 370 |

trogen. In the case when Mo is substituted for another metal the generalized cohesive energy is increased in substitutions of W and Nb, most in the case of Nb, and decreased for Ru. It is thus seen that the stabilization is greater for elements with lower valence and greater for 5*d* compared to 4*d* metals. This trend is in agreement with Ivanovskii and Shveikin[8] who found that the most effective stabilization of $\delta$-MoC with metal substitution may be reached for (i) lower valence metals and (ii) 4*d* metals as compared to 3*d* metals. The theoretical results are also in agreement with experiment for these ternary systems where one finds that both Nb and W have high solubility with the $\delta$-MoC phase while Ru does not.[15] One needs to remember that since there are always several competing possible phases for a given compound the fact that a certain structure is found to have a high cohesive energy does not necessarily imply that the compound will be found in this phase and that it is possible that a substitution will be accompanied by a phase transition.

### A. Equilibrium volumes and bulk moduli

The equilibrium volume is increased in the cases of boron and oxygen while it is decreased for nitrogen substitution. One also finds that the equilibrium volume is decreased in the case of ruthenium substitution but increased in the cases of niobium and tungsten, most for niobium.[16]

Hardness is one of the most technologically significant attributes of the transition-metal carbides. The hardness of a material is, however, not entirely given by the electronic structure but also depends on plastic deformation of the material and motion of dislocations. We thus caution the reader that the bulk modulus which is often regarded as a measure of hardness does not contain the full information on material hardness. However, a plot of hardness versus, e.g., bulk modulus for some of the technologically most interesting materials (BN, diamond, $RuO_2$) shows a linear relationship.[17] Having said this, we list the calculated bulk moduli for MoC with the different substitutional impurities in Table II.

The bulk modulus is decreased by inclusion of boron and oxygen but is slightly increased by the inclusion of nitrogen; this is probably strongly connected to the volume reducing effect of nitrogen inclusion in the carbon sublattice. This is so since, generally, a reduction of volume together with a maintained cohesive energy, which is the case for nitrogen inclusion, will give a stiffer material. That the inclusion of nitrogen in a transition-metal carbide increases the bulk modulus has also been found in TiC by Jhi and Ihm.[11] With metal substitutions the bulk modulus is decreased for both Nb and Ru substitutions but increased for substitution with W. This can be attributed to the fact that though the equilibrium volume is increased the cohesive energy is also increased resulting in a net effect of increased stiffness.

## IV. ELECTRONIC STRUCTURE

The density of states (DOS) is an important quantity for understanding the bonding in a compound. From the characteristic features of the density of states one can understand the bonding and the changes in the bonding upon substitution. One can also go further and make predictions about the effect of substitutional impurities using some simple models, one of which will be discussed in a coming section. A detailed study of the transfer of electronic charge is also made below.

### A. Density of states

In Figs. 3–5 the changes in the density of states is shown when 25% and 100% of the carbon is substituted for boron, nitrogen, or oxygen in $\delta$-MoC. The DOS for 100% substitution is shown in order to illustrate consistent trends in the DOS. Though it is of importance for the study of bonding trends to include MoB, MoN, and MoO it is good to keep in mind that of the structures studied here only MoC is found experimentally in the NaCl structure and that MoB, MoN, and MoO are not. In each figure the topmost DOS is for the $\delta$-MoC, the middle DOS is for 25% substitutional impurities, and the bottom DOS is for the 100% substitution. This allows a clear view of the changes in the DOS when substituting the carbon atoms. For the DOS of 25% substitutional impurities the partial DOS for only one of the two inequivalent Mo atoms is shown. The DOS for the other Mo atom contains, to a large extent, the same information. Figures 6–8 show the changes in density of states when 25% of the molybdenum is substituted for Nb, W, or Ru. As in the cases above there are two inequivalent carbon atoms but since they contain qualitatively the same information only one is displayed.

For the $\delta$-MoC phase we can divide the DOS into three main regions: I — a region of predominantly carbon *s* states with a small degree of hybridized *d* states from molybdenum, II — a region of hybridized carbon *p* states and molybdenum *d* states, III — predominately molybdenum *d* states with a small degree of hybridized *p* states from carbon. Region II can be viewed as the bonding part of the Mo-*d* nonmetal-*p* hybridization couples, while region III is the corresponding antibonding part. By studying differences and changes in these three regions we can extract valuable information concerning the bonding character and the changes in the bonding.

Starting with the nonmetals, the *s* states are shifted down in energy as we move from boron, through carbon and nitrogen to oxygen. This is due to the increased electronegativity of the atoms as we move across this series. There is also a downward shift in energy for the nonmetal *p* states and the energy split between the *s* and *p* states increases. The important hybridization between nonmetal *p* and molybdenum *d* states is retained but shifted in energies for substitution of boron and nitrogen while for oxygen this hybridization is

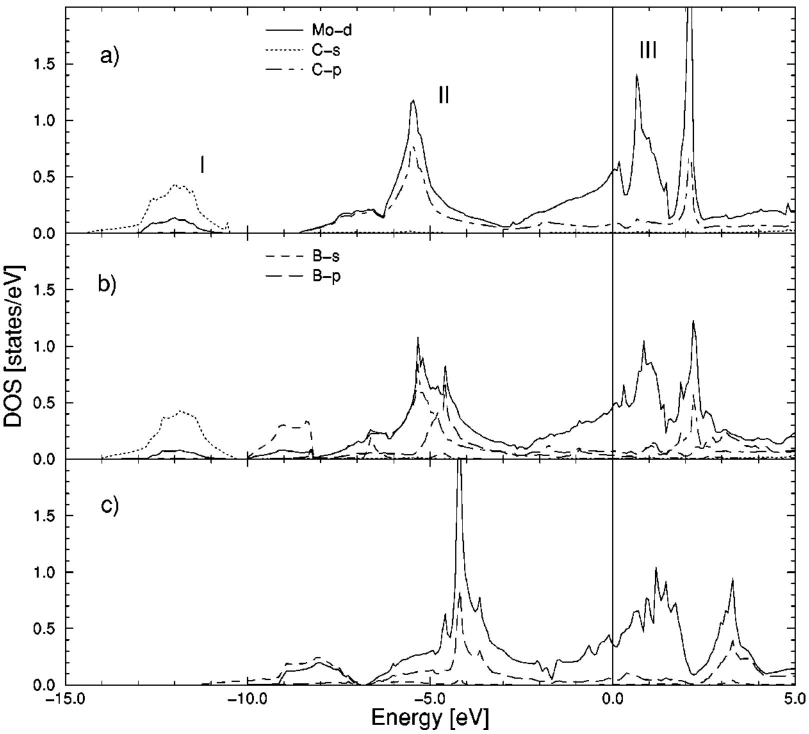

FIG. 3. Density of states for substitution with boron: MoC, $MoC_{0.75}B_{0.25}$, and MoB.

greatly decreased. This is reflected in the large decrease of cohesive energy for the systems with oxygen substitution. In order to understand why the cohesive energy is larger for the substitutional system with nitrogen than for the substitutional system with boron we note that though both systems retain hybridization between nonmetal *p* and molybdenum *d* states, in the case of boron these states are shifted up in energy while for nitrogen this shift is downwards, something which provides a stabilization mechanism. Our results for the changes in electronic structure from boron substitution are consistent with the ones found by Ivanovskii and Shveikin.[8] Comparing the cohesive energies of MoC and $MoC_{0.75}N_{0.25}$ it is evident that this downward shift does not compensate for the loss in relative hybridization between nonmetal *p* and molybdenum *d* states. In the case of O substitution the shift is even greater, but the *p*-*d* hybridization is reduced strongly

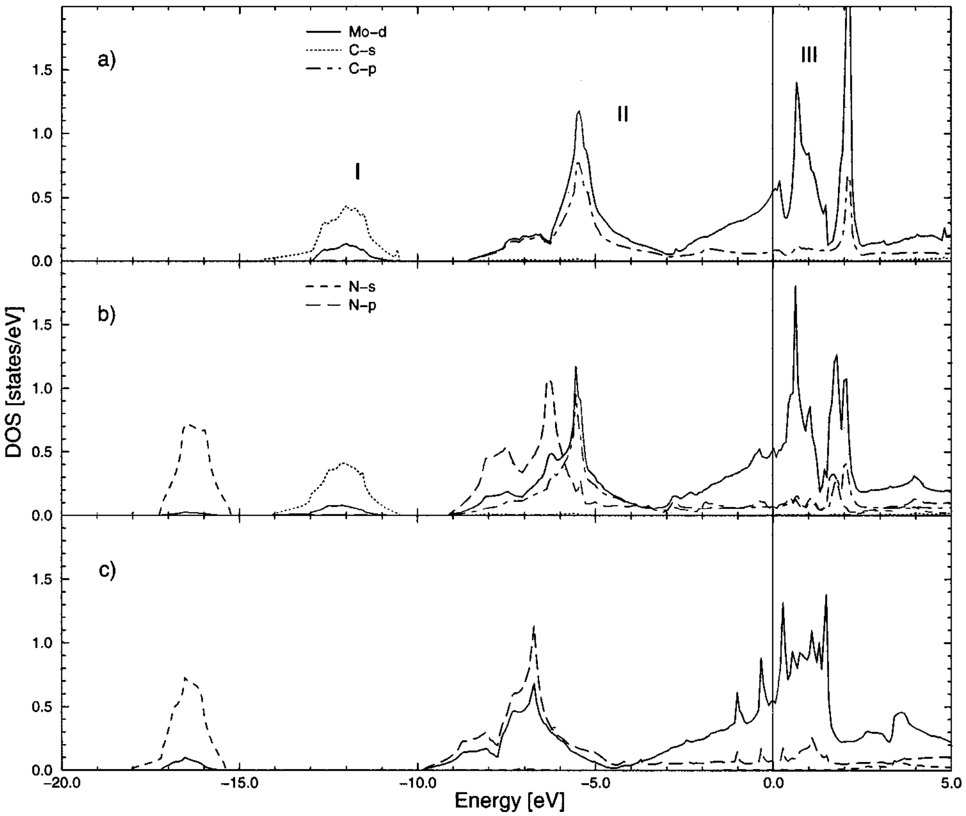

FIG. 4. Density of states for substitution with nitrogen: MoC, $MoC_{0.75}N_{0.25}$, and MoN.

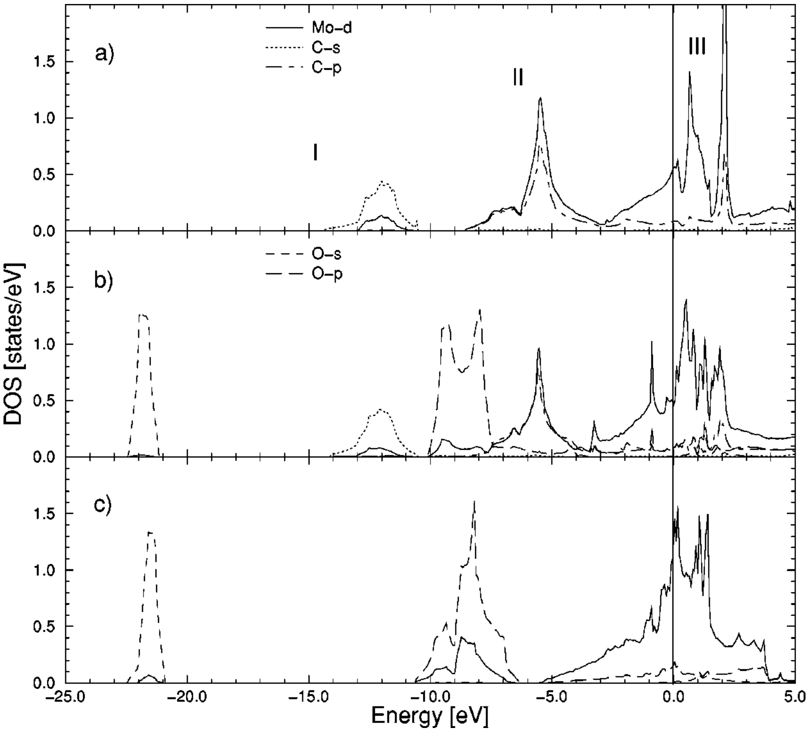

FIG. 5. Density of states for substitution with oxygen: MoC, $MoC_{0.75}O_{0.25}$, and MoO.

causing a weakening of the *p*-*d* bonds and decreased cohesive energy.[18]

In the case of metal substitution the changes in the DOS are much smaller and changing 25% Mo for Nb, apart from changing the Fermi level, only introduces some extra structure in the unoccupied metal *d* states. Substitution with W does not change the DOS in any significant way, as is expected since Mo and W are isoelectronic and chemically very similar. When studying Ru substitution we see a large difference in region III where the occupied *d* states for Ru differ from Mo states but otherwise the features are similar. Contrasting the changes in DOS for the nonmetal impurities with those of the metal impurities one finds that the DOS is significantly altered for nonmetal impurities with shifts of bands and widths and even the emergence of separate subbands while for metal impurities the DOS is largely unchanged. This effect has also been found in previous studies of impurities in TiC by Ivanovskii and co-workers.[3,9]

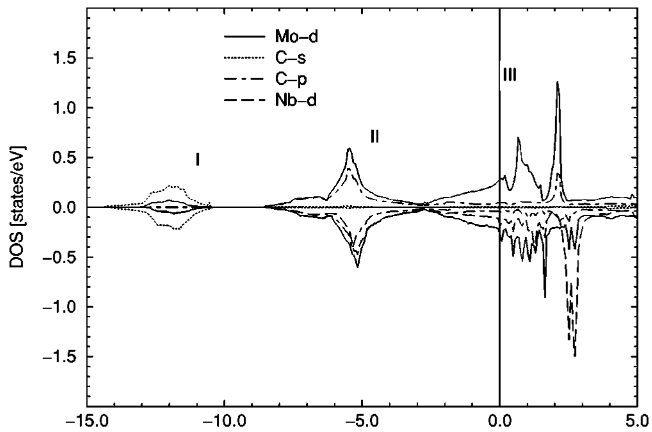

FIG. 6. Density of states for substitution with niobium: MoC, $Mo_{0.75}Nb_{0.25}C$ (mirrored).

### B. A rigid-band model

The DOS at the Fermi level $N(E_F)$ can provide an explanation, and sometimes a prediction, of the relative order of stability. That the order of structural stability sometimes correlates with $N(E_F)$ has, for instance, been found in Refs. 8 and 19. In the subsection above it was observed that the density of states is greatly changed by the inclusion of nonmetal impurities, so one would immediately say that a rigid-band model for predicting changes from the pure MoC to the compounds with nonmetal substitutions will not work while it should work better for the metal substitutions. Of course, a rigid-band model would predict no change when substituting Mo for W, and as seen above this is almost true. Though the rigid-band model is a simple model it is often used and therefore it is worthwhile to look closer at the predictions made and to see if and why it breaks down in the case of metal and nonmetal substitutions.

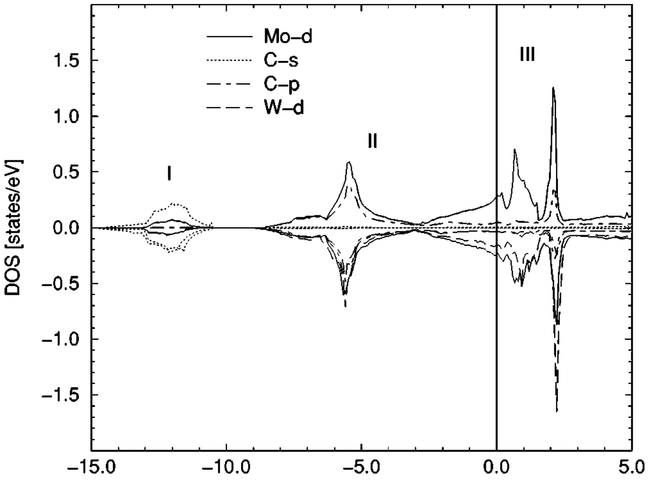

FIG. 7. Density of states for substitution with tungsten: MoC, $Mo_{0.75}W_{0.25}C$ (mirrored).

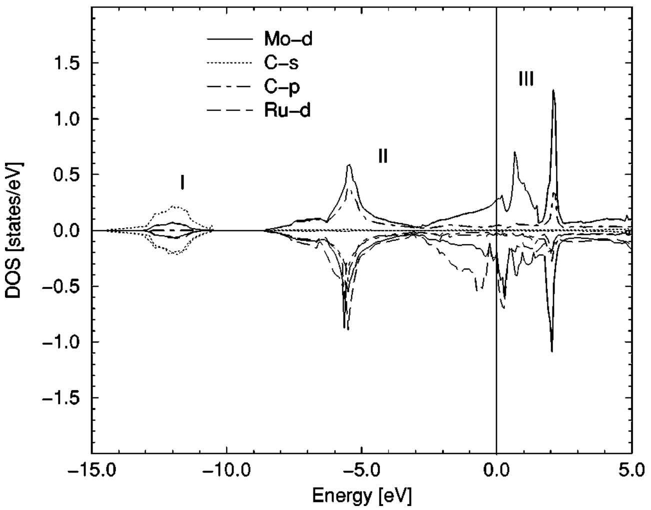

FIG. 8. Density of states for substitution with ruthenium: MoC, $Mo_{0.75}Ru_{0.25}C$ (mirrored).

In a rigid-band model for predicting the changes in structural stability for 25% substitution the $N(E_F)$ is compared with the DOS at 0.25 fewer electrons in the valence band (for boron/niobium), 0.25 more (nitrogen), and 0.50 more (oxygen/ruthenium). This procedure is illustrated in Fig. 9 and the predicted $N(E_F)$ can be compared to the calculated $N(E_F)$ from Figs. 3 to 8. In Nb substitution, as predicted, $N(E_f)$ is decreased and for Ru substitution the DOS is expected to move into a valley or just to the edge of a peak and this is also seen to be the case. In both cases the predictions of the rigid-band model turn out to be correct for metal substitutions. Substitution with Ru does, however, influence the stability of the compound though it does not significantly change $N(E_F)$. For nonmetal substitution it is different; with boron a rigid-band model predicts that $N(E_F)$ is slightly decreased, but from Fig. 3(b) the actual $N(E_F)$ is not significantly changed. For substitution of nitrogen and oxygen the $N(E_F)$ is expected to move down from a peak to a small valley but, from Figs. 4 and 5, this region is filled with Mo *d* states and $N(E_F)$ is once again not significantly changed. The expected, from rigid-band arguments, decrease in $N(E_F)$ is therefore never realized.

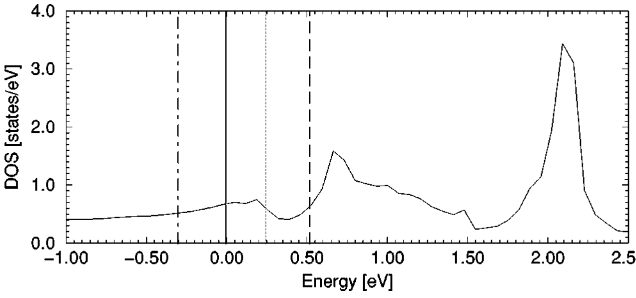

FIG. 9. DOS at the Fermi level from rigid-band reasoning for $\delta$-MoC with substitutional impurities. The solid line denotes the Fermi level for MoC. The dot-dashed line shows the Fermi level for $MoC_{0.75}B_{0.25}$ (equivalently $Mo_{0.75}Nb_{0.25}C$), the dotted line for $MoC_{0.75}N_{0.25}$, and the long dashed line for $MoC_{0.75}O_{0.25}$ (equivalently $Mo_{0.75}Ru_{0.25}C$).

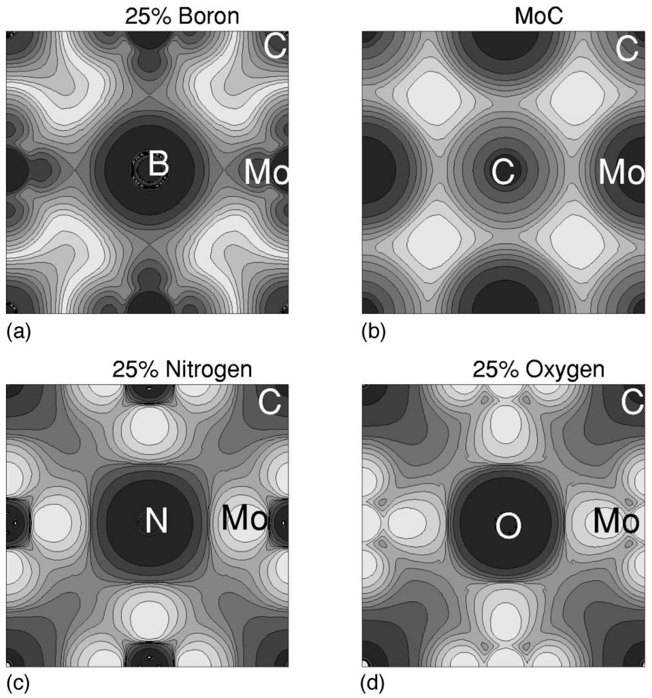

FIG. 10. Difference in electron density (a) $MoC_{0.75}B_{0.25}$ minus MoC, (c) $MoC_{0.75}N_{0.25}$ minus MoC, and (d) $MoC_{0.75}O_{0.25}$ minus MoC. The electron density of MoC is shown in (b) for reference. The positions of the atoms are indicated in the figure. The cuts have been made in the (001) plane. The contours are shaded from dark to light, dark being the areas with largest difference in electron density from the reference MoC.

### C. Charge density

To more clearly illustrate the trends in bonding when going from substitution of boron to substitution of oxygen we have studied the changes in electronic density in the crystal by taking the difference between the charge densities of the substitutional compound and the charge density of MoC, e.g., the charge density of MoC is subtracted from that of $MoC_{0.75}B_{0.25}$ to see the characteristics of the changes in charge density (e.g., ionic versus covalent) and where in space the changes are most pronounced. In Figs. 10 and 11 these differences are displayed in a plane of the crystal. In both figures the electron density of MoC is shown for reference. The position of the atoms are indicated in the figures. The contours are shaded from dark to light, the darker the contour the larger the change in electron density from that of the reference state . Note that the difference is taken between calculations with different number of electrons with the reference point always being the MoC charge density. In the case of alloy substitutions with a smaller number of valence electrons the lightest shaded contour represents a small depletion and the darkest shaded contour shows a larger depletion of electrons. In the case of alloys with higher valence electron density dark contours represent a large surplus of electron density and lighter contours show areas with a smaller surplus.

Figure 10 shows that in a substitution of carbon for boron the largest change in electron density is from a highly covalent *p*-*d* bond which in the substituted system is between B and Mo atoms. For nitrogen substitution most of the extra charge is found at the nitrogen atom and the structure of the

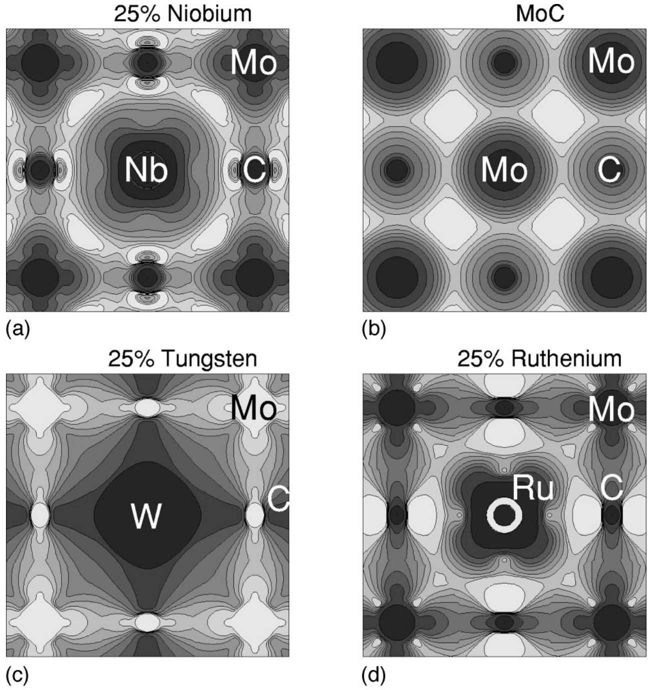

FIG. 11. Difference in electron density (a) $Mo_{0.75}Nb_{0.25}C$ minus MoC, (c) $Mo_{0.75}W_{0.25}C$ minus MoC, and (d) $Mo_{0.75}Ru_{0.25}C$ minus MoC. The electron density of MoC is shown in (b) for reference. The positions of the atoms are indicated in the figure. The cuts have been made in the (001) plane. The contours are shaded from dark to light, dark being the areas with largest difference in electron density from the reference MoC.

electron density difference is different from the B substitution. In particular it may be seen that the extra valence electron accompanying the N substitution enters orbitals which are centered on the N atom. Hence substituting C for N increases the ionic component of the chemical bond. This is also the case for oxygen substitution, where the tendency for an ionic component to the bonding is even larger, since Fig. 10 shows that the extra valence electron charge is almost entirely located on the O atom. The charge contour plots discussed in Fig. 10 show that the nature of the bonding characteristics for the electron which is removed or added when we substitute C for B, N or O, is neither completely ionic, covalent, or metallic. If the bonding had been metallic then the charge density would be removed (or added) in a more uniform manner over the entire crystal interstitial. If the bonding had been entirely covalent the charge would be removed (or added) only from the bonds between the atoms, and if the bonding was ionic we would find all the surplus (or depletion) on atomic sites. In our case we observe a mixture of all these archetypal bonding characteristics but the trends are clear that Mo binds more covalently to B and C whereas the ionicity becomes more important especially for O substitution. This is a clear indication of the increased electronegativity when going from boron to oxygen in combination with the *p*-bands becoming less extended as we traverse the series. This results in a smaller overlap with the Mo atom and a reduced covalent bonding.

For metal substitutions the differences in charge density are shown in Fig. 11. For 25% Nb substitution the electron density is removed both from the Mo atom as well as from the carbon-molybdenum covalent *p-d* bond. When substituting for W charge is shifted from the carbon and Mo atoms and the bond between them to the W atom and the tungsten-carbon bond. For Ru substitution charge is accumulated on the Ru atoms and on the Mo-C covalent *p-d* bond. From the DOS in Fig. 8 it is also seen that the states occupied when substituting Mo for Ru have *d* character. Figure 8 also clearly shows that the electronic states on the Ru atom are isolated with clear minima in the electronic density between the Ru atom and its neighboring C and Mo atoms, illustrating why the filling of these states does not increase the bonding in the compound. Comparing the effect of niobium and ruthenium substitution, electrons are removed or added to a covalent *p-d* bond with only a smaller component of charge transfer.

To summarize this section the charge density contours give a picture which is consistent with the analysis based on the density-of-states curves, i.e., that the chemical bonding in this class of materials has a large covalent *p-d* component which is maximized in strength for alloy concentrations close to MoC. This covalent bonding is accompanied with metal *d-d* bonding and an ionic component which grows in strength for the more electronegative anions.

## V. THE QUATERNARY ALLOY $Mo_{0.75}W_{0.25}C_{0.75}N_{0.25}$

Following up our results that both a substitution with nitrogen and one with tungsten lead to a slightly increased bulk modulus, it is natural to study the quaternary alloy $Mo_{0.75}W_{0.25}C_{0.75}N_{0.25}$. The equilibrium volume of this alloy is found to be 20.192 Å$^3$, the cohesive energy 21.783 eV, and the bulk modulus 370 GPa. This alloy thus has a smaller equilibrium volume than MoC, a smaller cohesive energy, and a slightly larger bulk modulus, only of the order $1-2\,\%$. Though the increase in bulk modulus is not large this is a compound that retains the high bulk modulus of MoC and might have other qualities that could be of interest and worthy of experimental study.

## VI. CONCLUSION

We have studied the cohesion and electronic structure of MoC with substitutional impurities of nonmetal boron, nitrogen, and oxygen and metal niobium, tungsten, and ruthenium using first-principles full-potential LMTO calculations.

Examination of the electronic structure and charge density gives an explanation to the trends in cohesive energies, equilibrium volumes, and bulk moduli. The results from changes in the energy and equilibrium volumes are contradictory to simple pictures of the nature of the bonding in these compounds. In order to further understand the ionic, covalent, or metallic nature of the bonding a study of the changes in DOS and charge density shows that the chemical bonding between anion and cations in this class of materials changes from being dominated by covalent *p-d* bonding for B and C to a more ionic bonding for the more electronegative compounds, especially the oxide. The maximum cohesive energy and minimum equilibrium volume for a band filling somewhere between MoC and MoN are thus an effect of the fact that for these band fillings the covalent *p-d* bonds start to weaken and are replaced by a weaker more ionic component of the chemical bonding which becomes quite strong for the oxides. This situation is likely to occur also for other transition-metal carbides, nitrides, and oxides and our analysis is in certain aspects consistent with the analysis of Gelatt, Williams, and Moruzzi, who found a decrease in the $p$-$d$ bonding when the valence states of the constituent atoms become less degenerate.[18] However, our analysis is somewhat in conflict with the work of Price and Cooper who came to the conclusion when comparing TiC and WC that the two additional $d$ electrons in WC engage in W-W metallic bonding rather than W-C covalent bonds.[20]

The trend that $\delta$-MoC is stabilized more by the lower valance element and more by the $5d$ compared to $4d$ metals complies with the order found previously by Ivanovskii and Shveikin.[8] and with experimental results on these ternary systems.[15] Our studies show that the nonmetal substitution which retains the highest cohesive energy is nitrogen and that this also increases the bulk modulus of the compound, indicating that such a substitution might increase the macroscopic hardness of $\delta$-MoC. Our studies of metal substitutions show that replacement with W increases the bulk modulus of $\delta$-MoC. Combining this with the effect of nitrogen substitution the quaternary alloy $Mo_{0.75}W_{0.25}C_{0.75}N_{0.25}$ has been studied and found to be a material with similar volume to $\delta$-MoC and slightly increased hardness that could be a candidate for technological applications.

## ACKNOWLEDGMENTS

This work has been supported by the Swedish Natural Science Research Council (NFR and TFR). We are grateful to Dr. J.M. Wills for supplying his FP-LMTO code. Fruitful discussions with Dr. M.S.S. Brooks are also acknowledged.

---

[1] S.T. Oyama, Catal. Today **15**, 179 (1992).

[2] J. Wood, J.E. Kern, J.T Kern, A.M. Kedin, R.W. Burkhardt, and S.R. Ovshinsky, IEEE Trans. Magn. **21**, 842 (1985); E.L Haase, J. Low Temp. Phys. **69**, 245 (1987); J. Lu, H. Hugosson, O. Eriksson, L. Nordström, and U. Jansson (unpublished).

[3] A.L. Ivanovskii, D.L. Novikov, V.I. Anisimov, and V.A Gubanov, J. Phys. Chem. Solids **49**, 487 (1988).

[4] J.L. Calais, Adv. Phys. **26**, 1847 (1977).

[5] A. Neckel, Int. J. Quantum Chem. **XXIII**, 1317 (1983).

[6] L.I. Johansson, Surf. Sci. Rep. **21**, 177 (1995).

[7] K. Schwarz, CRC Crit. Rev. Solid State Mater. Sci. **13**, 3 (1987).

[8] A.L. Ivanovskii and G.P. Shveikin, Phys. Status Solidi B **181**, 251 (1994).

[9] A.L. Ivanovskii, D.L. Novikov, V.I. Anisimov, and V.A Gubanov, J. Phys. Chem. Solids **49**, 479 (1988).

[10] H. W. Hugosson, O. Eriksson, L. Nordström, U. Jansson, L. Fast, A. Delin, B. Johansson, and J. M. Wills, J. Appl. Phys. **86**, 7 (1999).

[11] S. Jhi and J. Ihm, Phys. Rev. B **56**, 13 826 (1997).

[12] J. M. Wills (unpublished).

[13] H. Skriver, *The LMTO Method*, Springer Series in Solid State Sciences Vol. 41 (Springer Verlag, Berlin, 1984).

[14] The relaxations should be of the order a few mRy. Relaxations around a vacancy site in Mo are of the order 1–2 mRy; B. Meyer and M. Fähnle, Phys. Rev. B **56**, 13 595 (1997).

[15] P. Villars, A. Prince, and H. Okamoto, *Handbook of Ternary Alloy Phase Diagrams* (ASM International, Materials Park, OH 1995); J. Shuster and H. Novotny, Monatsch. Chem. **110**, 231 (1979).

[16] A comparison between theoretical and experimental volumes would not be relevant since the only experimental data available are for substoichiometric $\delta$-MoC. Recent studies of stoichiometric and substoichiometric MoC have found good agreement between theoretical and experimental volumes. (Ref. 10)

[17] J.M. Legér and B. Blanzat, J. Mater. Sci. Lett. **13**, 1688 (1994).

[18] The bonding in a transition-metal compound has been shown to result from a competition between a weakening of the transition-metal $d$-$d$ bonds by the dilation of the lattice and increased bonding due the occupation of hybridized states of interaction between metal $d$ and nonmetal $s$ and $p$ bonds; C.D. Gelatt, A.R. Williams, and V.L. Moruzzi, Phys. Rev. B **27**, 2005 (1983).

[19] D. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford University Press, New York, 1995).

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