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Elastic and Piezoresistive Properties of Nickel Carbides from First-Principles

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The nickel–carbon system has received increased attention over the past years due to the relevance of nickel as a catalyst for carbon nanotube and graphene growth, where Nickel carbide intermediates may be involved or carbide interface layers form in the end. Nickel–carbon composite thin films comprising Ni_3C are especially interesting in mechanical sensing applications. Due to the metastability of nickel carbides, formation conditions and the coupling between mechanical and electrical properties are not yet well understood. Using first-principles electronic structure methods, we calculated the elastic properties of Ni_3C , Ni_2C and NiC , as well as changes in electronic properties under mechanical strain. We observe that the electronic density of states around the Fermi level does not change under the considered strains of up to 1%, which correspond to stresses up to 3 GPa. Relative changes in conductivity of Ni_3C range up to maximum values of about 10%.

I. INTRODUCTION

Nickel–carbon compounds and composite thin films containing amorphous carbon are of high interest for various applications. Thin films have been investigated for their piezoresistive properties¹ and as low friction solid lubricants². The meta-stable Ni_3C has been frequently observed in such films^{3–5} and was suggested to cause piezoresistive behaviour¹. This carbide has been reported to be hard to distinguish from hcp-nickel, where a study⁵ suggests that hcp-nickel is only stable in the presence of carbon and with some carbon content. A meta-study on this subject can be found in reference 4. A recent study⁶ confirmed, that Ni_3C in such films only decomposes at temperatures well above 250 °C.

The nickel–carbon system is also of interest for the catalytic production of carbon nanotubes (CNTs) and graphene. CNT-growth was achieved both using nickel nanoparticles as a catalyst^{7,8} and on carbon–nickel nanocomposite thin films⁹. While studies suggest, that carbides do not form during CNT growth from Ni nanoparticles¹⁰, Ni_3C has been observed in nanoparticles after CNT growth by plasma enhanced chemical vapor deposition was stopped¹¹. A more recent study¹² confirmed, that Ni/ Ni_3C core-shell structures can indeed be produced. In such a setup, the carbide could act as an advanced contact material for CNT junctions with properties similar to those demonstrated for Mo_2C ¹³. The advantage would be, that the Ni_3C –CNT unit can be grown bottom-up. Ni_3C does also occur as a parasitic by-product of carbon nanofiber-growth on nickel foam¹⁴.

Graphene¹⁵ and graphene–type interfacial layers¹⁶ can be produced by metal-induced crystallization and layer inversion as well as by epitaxial growth on transition metals, such as nickel¹⁷. In the latter case, one study¹⁸ excluded the occurrence of crystalline Ni_3C on a poly-

crystalline Ni surface by XRD measurements. Others observed an interface layer between {111}-nickel and graphene with the stoichiometry Ni_2C by Auger spectroscopy^{19,20}. In both cases, mechanical details, especially of carbide intermediates require further study.

The stability of a range of nickel–carbides has been investigated by density functional calculations²¹, yet, neglecting the influence of elastic deformations which we address here. The study confirmed that, without externally induced strains, Ni_3C in space group 167 structure, figure 1(c), is the least unstable carbide and suggests that Ni_2C is most stable in orthorhombic structures of space groups 058 ($Pnmm$) and 060 ($Pbcn$), see figures 1(a) and (b).

All in all, especially the phase Ni_3C has potential technical applications in heterojunctions consisting of nickel and carbon allotropes, including CNTs, acting as electrical circuit elements, for example piezoresistive sensors²². In these applications, the mechanical and piezoresistive properties of a potential carbide layer between nickel and the carbon structure can become relevant when the device is being strained during operation or when the layer is under constant epitaxial stress which may be caused the large surface tension of nickel²³.

The present work focuses on investigating the elastic properties of the three nickel carbides NiC , Ni_2C and Ni_3C in their most stable crystallographic structures. Ground state properties of the carbides are compared in section III A, the obtained elastic properties are discussed in section III B. For the experimentally most relevant carbide, Ni_3C , the influence of strain on the electronic transport properties is discussed in section III C.

II. COMPUTATIONAL METHODS

A. Electronic Structure Calculations

NiC was calculated in rocksalt (B1) structure, for Ni_2C the structures proposed by Gibson et al.²¹ were used and for Ni_3C the rhombohedral (bainite, space group 167) structure, which was experimentally found by Nagakura²⁴ was assumed (see figure 1(c)).

All results presented here were obtained applying density functional theory (DFT), in the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) parametrization²⁵ as exchange–correlation functional, which is known to give good results for bulk mechanical properties when comparing to experiments²⁶. The plane-wave implementation in the ABINIT package^{27–29} was used, employing the projector augmented wave (PAW) method³⁰. The PAW atomic data sets treat $3d^8 4s^2$ and $2s^2 2p^2$ as valence for nickel³¹ and carbon³², respectively.

For numerical accuracy, the plane-wave cutoff was converged to $E_{\text{cut}} \sim 980 \text{ eV}$ ($= 36 \text{ Ha}$). Only, for calculations of fcc-nickel, the cutoff was set to about 1360 eV (50 Ha) in order to reach a convergence of total energy below about 2.7 meV ($1 \times 10^{-4} \text{ Ha}$) per atom. At this point

energy differences under strain are converged to below about $0.27 \mu\text{eV}$ ($1 \times 10^{-8} \text{ Ha}$), which is far more accurate than required for structural relaxation and the calculation of elastic properties. The stronger total energy criterion was chosen with regard to calculating formation enthalpies.

When calculating ground state properties of carbides the Brillouin zone was sampled with a Monkhorst–Pack grid of $12 \times 12 \times 12$ k -points. Thermal smearing of Fermi–Dirac-type³³ was fixed to about 27 meV ($1 \times 10^{-3} \text{ Ha}$). Since the unit cells of nickel and diamond are smaller, denser grids of $32 \times 32 \times 32$ and $16 \times 16 \times 16$ k -points, respectively, were required in order to get comparable sampling accuracy.

The ground state formation energies per formula unit (f.u.) for the carbides were calculated according to

$$\Delta E_f = E_{\text{Ni}_x\text{C}_y} - x E_{\text{fcc-Ni}} - y (E_{\text{diamond}} - 25 \text{ meV}) \quad (1)$$

where E_i is the total energy of compound i . Diamond was calculated as carbon reference structure instead of graphite because the employed method is not capable of correctly calculating van-der-Vaals interactions. An empiric correction of $\Delta E_C = 25 \text{ meV}$ per carbon atom, also used in reference 21, was applied to obtain formation energies with respect to graphite.

B. Frozen Phonon Calculations

Within the linear regime, elastic properties can be described by the elastic tensor \hat{C} , which gives the stress response $\hat{\sigma}$ of a material proportional to a deformation \hat{e} :

$$\sigma_i = \sum_j c_{ij} \cdot e_j \quad (2)$$

Here, Voigt’s notation is used to write the stress and deformation tensors as six-vectors ($11 \rightarrow 1$; $22 \rightarrow 2$; $33 \rightarrow 3$; $23 \rightarrow 4$; $13 \rightarrow 5$; $12 \rightarrow 6$), with entries corresponding to three axial strains (1–3) and shear strains (4–6). In this way the elastic tensor can be written as a 6×6 matrix from which all elastic properties can be derived. The bulk modulus is given by:

$$B = \frac{1}{3} (\langle c_{11} \rangle + 2 \langle c_{12} \rangle) \quad (3)$$

where $\langle c_{11} \rangle$ denotes an average over the diagonal axial strain entries and $\langle c_{12} \rangle$ an average over the off-diagonal axial strain entries.

The entries of the elastic tensor were calculated using the frozen phonon (FP) method, where the stress-response was derived from ground state calculations of the deformed primitive cell. A more detailed explanation can be found in³⁴. The six primitive deformations were applied separately with magnitudes ranging up to 1%. All elastic constants were then determined using equation (2). The diagonal entries of the tensor can also

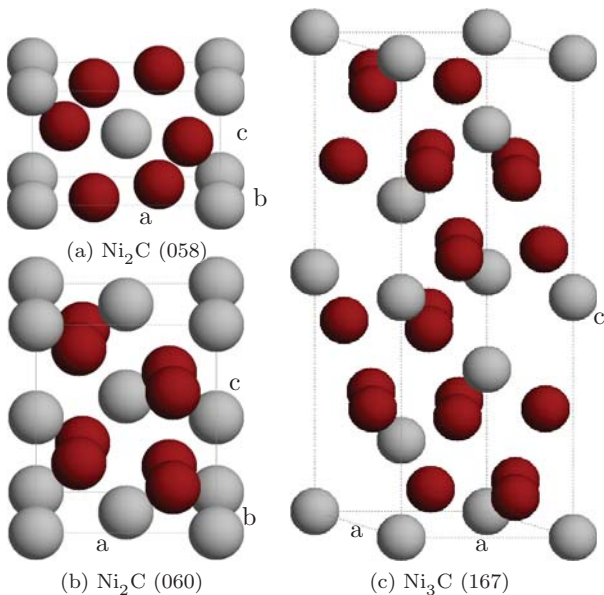


FIG. 1. (color online) Overview of the crystal structures used in this work for Ni_2C of space groups 058 ((a), two f.u.) and 060 ((b), four f.u.), both orthorhombic, as well as of Ni_3C ((c), space group 167, six f.u.). The latter is displayed in a hexagonal unit cell for clarity, where the angle enclosed by the a edges in the basal plane is equal to 120° . A primitive rhombohedral cell of only one third the size exists which was used for calculations. The grey balls represent carbon and the red ones represent nickel. The unit vector \mathbf{e}_x is always parallel to a and \mathbf{e}_z is parallel to c .

be determined from the total energies of the same calculations:

$$E_\delta = E_0 + \frac{V_0}{2} \sum_i c_{ii} \cdot e_i^2 \quad (4)$$

where E_0 and V_0 are the total energy and volume of the unstrained cell. The calculated tensors were checked for consistency by comparing the results of equations (2) and (4). The calculation parameters were converged until the difference between the diagonal tensor elements from both equations was less than 2 GPa. This criterion called for using a $48 \times 48 \times 48$ k -point grid for the deformed cell of NiC, for the other materials it was met by using the aforementioned simulation parameters.

If the material's unit cell exhibits internal degrees of freedom, performing a ground state calculation of the deformed cell without relaxation of the ion positions yields entries of the so-called *clamped-ion* elastic tensor \hat{C}^c . To obtain the more physical *relaxed-ion* elastic tensor \hat{C}^r , the internal atomic coordinates were relaxed using the Broyden–Fletcher–Goldfarb–Shanno algorithm as implemented in ABINIT until all forces were below 5×10^{-4} eV/Å.

C. Electronic Transport

Electronic transport was calculated assuming constant relaxation time τ within the Boltzmann formalism where the conductivity tensor at zero temperature is given as:³⁵

$$\zeta_{ij} = \tau \frac{e^2}{(2\pi)^3 \hbar} \sum_n \int_{\varepsilon^n(\mathbf{k})=E_{\text{Fermi}}} dS \frac{v_i^n(\mathbf{k})v_j^n(\mathbf{k})}{|\mathbf{v}^n(\mathbf{k})|} \quad (5)$$

$$\text{with } \mathbf{v}^n(\mathbf{k}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} \varepsilon^n(\mathbf{k})$$

where ε^n is the eigenenergy of the n th band and $\mathbf{v}^n(\mathbf{k})$ the vector of the corresponding group velocity. e denotes the electron charge and i, j denote cartesian vector components.

Off-diagonal elements of ζ_{ij} are zero by symmetry. For the relaxation time τ no specific value is assumed, though it might be anisotropic ($\tau_{zz} \neq \tau_{xx} = \tau_{yy}$) in the case of Ni₃C due to its rhombohedral structure³⁶. The integrals on the right-hand side of equation (5) reflect the anisotropy of the bandstructure of the unperturbed, but eventually strained, systems at the Fermi level. Assuming that τ remains constant under strain in the linear regime, since no new scattering centers are created, predictions can be made about the change of conductivity under strain.

For strained cells, the bandstructure with relaxed ion positions was used as basis for these calculations.

III. RESULTS AND DISCUSSION

A. Ground State Results

The lattice parameters of the investigated materials are available in literature, some even from experiments. The lattice constant calculated for fcc-nickel in the present work ($a_{\text{Ni}} = 3.524$ Å) agrees very well with values found in literature^{21,37}. The obtained lattice parameter for diamond ($a_{\text{diamond}} = 3.577$ Å) is only slightly larger than the experimental value of 3.567 Å³⁸. Lattice parameters obtained for the carbides as well as formation enthalpies will be given for comparison, the latter with respect to fcc-Ni and graphite.

a. NiC Assuming rocksalt structure, the lattice parameter $a_{\text{NiC}} = 4.073$ Å was obtained, which is in good agreement with ref.²¹ (4.077 Å) and other numerical studies cited therein. The calculated formation enthalpy of $\Delta E_{f,\text{NiC}} = 49.7$ kcal/mol of f.u. also agrees with ref.²¹ (48.6 kcal/mol).

TABLE I. Lattice parameters, formation enthalpies and total energies for the two considered orthorhombic structures of Ni₂C. Length values are given in Å, formation enthalpies in kcal/mol of f.u. Values from ref.²¹ are given in parentheses.

	Ni ₂ C (058)	Ni ₂ C (060)
a	4.72(4.72)	4.19(4.19)
b	4.19(4.17)	5.51(5.51)
c	2.93(2.92)	4.94(4.94)
ΔE_f	12.2(7.9)	12.0(7.9)

b. Ni₂C The calculated values for the two investigated structures are summarized in table I. The lattice parameters are in excellent agreement with ref.²¹. Only, the formation enthalpies stated therein disagree with the present results (see table I, values in parentheses). However, there is agreement on the prediction that both structures are essentially degenerate, with the variant of space group 060 being less than 5 meV lower in total energy.

c. Ni₃C The obtained lattice parameters $a = 4.60$ Å and $c = 13.00$ Å are in good agreement with ref.²¹ ($a = 4.49$ Å, $c = 13.02$ Å) and electron diffraction measurements³⁹ ($a = 4.553$ Å, $c = 12.92$ Å). A formation enthalpy of $\Delta E_{f,\text{Ni}_3\text{C}} = 6.3$ kcal/mol was obtained, which is identical to the value reported in ref.²¹ and reflects the thermal decomposition observed in⁴⁰.

For the relaxed, strain-free geometries, all carbides of nickel investigated here are meta-stable at $T = 0$ K, non-magnetic and metallic as observed previously²¹. Ni₂C exhibits a very low density of states (DOS) around the Fermi energy. The DOS for the investigated carbides and the reference phases are plotted in figure 2.

In all carbides the C 2s band is located below the conduction band. It is shifted to lower energies (shifted left in figure 2) for Ni₂C and Ni₃C in comparison to the carbide with higher carbon content, NiC, indicating a deeper

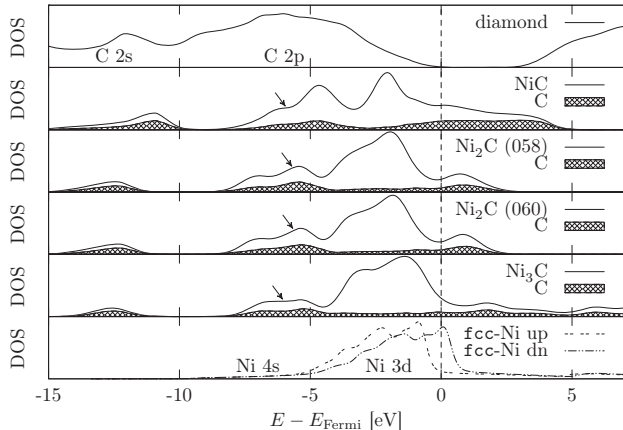


FIG. 2. Total and projected DOS of carbides compared to those of the reference phases. For display, Gaussian smearing of about 270 meV (1×10^{-2} Ha) was applied. Atomic orbitals are indicated as obtained from calculations of projected DOS, filled areas under curves indicate the fraction of DOS attributed to C sites. The arrows indicate the bonding band with C 2p and hybrid Ni states.

potential well for electrons is provided by the carbon atoms. They are also more strongly negatively charged than in NiC. The Ni 3d states are located below the Fermi energy above about -5 eV for Ni_2C and Ni_3C , for NiC they are spread over a broader energy range, starting at around -6 eV. The Ni 3d orbitals do contribute to the DOS at the Fermi level, but much less than in fcc-nickel, where the 3d-DOS of the minority spin peaks at the Fermi level. Ni 4s and C 2p states also contribute to the DOS at the Fermi level. The part of the conduction band below about -5 eV is predominately composed of C 2p states hybridizing with Ni states, see arrows in figure 2.

B. Elastic Constants

As a reference, the elastic tensors of fcc-Ni and diamond were calculated and the non-zero, not symmetrically equivalent elements are provided in table II. The calculated bulk modulus for diamond is identical to earlier theoretical works⁴¹ and also the tensor components agree with earlier literature data⁴². The bulk modulus for Ni is within about 10 GPa of experimental results⁴³. This deviation is predominantly attributed to the approximations involved in DFT. The following predictions for the elastic properties of nickel carbides can be expected to have about the same accuracy.

All carbides exhibit a larger bulk modulus than Nickel and a much lower one than diamond, as apparent from the last column of table II. Being the carbide with the highest carbon content, NiC shows the largest bulk modulus of the carbides. Evidently, the bulk modulus increases with increasing carbon content, that is, the sub-

stances become harder. Table II lists all calculated non-zero and not symmetrically equivalent elastic constants. The carbides Ni_2C and Ni_3C exhibit less symmetric unit cells, resulting in more independent entries in the elastic tensor.

a. Ni_2C Both investigated hypothetical forms of Ni_2C are predicted to be equally hard and even show quite similar anisotropies, probably due to the fact that both are orthorhombic. The elastic properties of the sample should not depend on the relative prevalence of these two phases. Still, judging by the elastic tensors, deforming one cell into the equilibrium shape of the other and allowing the atoms to rearrange into the other structure by relaxation requires overcoming a large potential barrier. Thus, even under stress, both structures can be expected to coexist in one sample.

b. Ni_3C Judging by the obtained bulk moduli, a macroscopically isotropic polycrystalline sample of Ni_3C is predicted to be about as hard as the less stable Ni_2C . Even for the most extreme simulated deformations of 1% stresses were found to be still in the linear regime. Using the calculated value for c_{11}^r , a compression in \mathbf{e}_1 -direction of this magnitude corresponds to applying a pressure of about 2.7 GPa, which by far exceeds pressures achievable in most experiments.

Investigating DOS and band structure of deformed cells, no qualitative difference with respect to that obtained for the equilibrium geometry was found. For purely axial strains and compressions (i.e. \mathbf{e}_1 , \mathbf{e}_2 and \mathbf{e}_3 , see figure 3(b)) bands move slightly closer to the Fermi-level under strain and further away under compression. This can be attributed to changing overlaps between atomic orbitals. This difference is marginal close to and at the Fermi level, the region most relevant to transport properties. For pure shear deformations no significant changes are observed, see figure 3(c). Band structures shown in figure 3 for deformed cells use relaxed ion positions. Clamped cells show qualitatively identical changes, only the shift of bands for strains and compressions is larger.

C. Electronic Transport under Strain

A closer analysis of the Ni_3C band structure yields a density of states of 2.83 eV^{-1} per f.u. and anisotropic averaged Fermi velocities of $v_x = v_y = 0.90 \times 10^6$ m/s and $v_z = 1.10 \times 10^6$ m/s. This results in an in-plane/out-of-plane conductivity anisotropy of about 0.67.

The respective effect of axial strains in x and z direction (\mathbf{e}_1 and \mathbf{e}_3) on electronic transport was investigated. For strains up to $\pm 1\%$ the DOS remains unaffected within the precision of the calculation. Table III summarizes relative changes under strain in both conductance and Fermi velocities. The strongest changes in conductance can be observed for strains along \mathbf{e}_3 , where the parallel conductance in z direction changes by 10%, the anisotropy increases slightly. For small strains along

TABLE II. Calculated elastic constants, c_{ij} and bulk modulus B , for the considered carbide phases and the reference phases diamond and fcc-Nickel in GPa. For phases with atomic degrees of freedom on the unit cell (Ni_2C , Ni_3C) both clamped-ion and relaxed-ion results are listed. All omitted entries are given by or are zero by symmetry. For space group 167 (Ni_3C) the following relation holds: $c_{56} = c_{14} = -c_{24}$.

	c_{11}	c_{22}	c_{33}	c_{12}	c_{13}	c_{23}	c_{44}	c_{55}	c_{66}	c_{14}	B
diamond	1049			129			564				435
NiC	296			231			50				256
Ni_2C (058), clamped	316	262	378	218	175	193	116	91	145		236
Ni_2C (058), relaxed	307	234	344	203	160	163	88	87	145		215
Ni_2C (060), clamped	279	343	359	213	203	171	90	125	135		239
Ni_2C (060), relaxed	251	333	335	205	186	163	78	91	113		225
Ni_3C clamped	321		309	176	184		116		72	-11	227
Ni_3C relaxed	272		276	157	150		91		57	-22	219
fcc-Ni	266			156			129				192

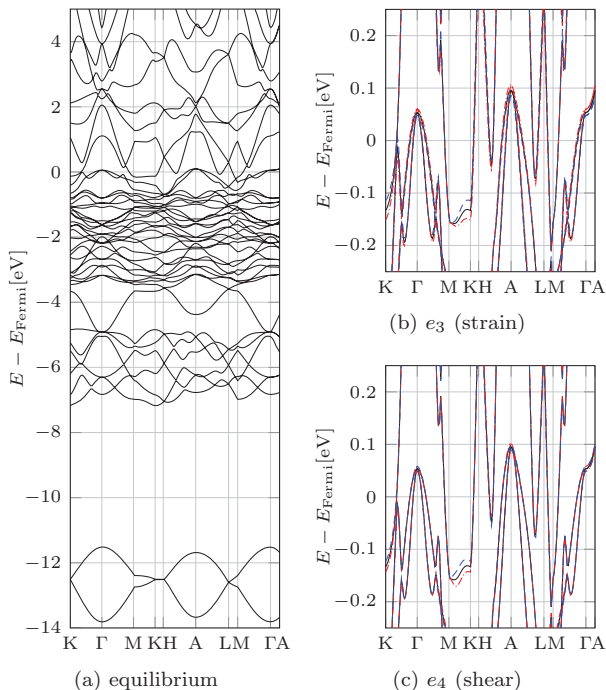


FIG. 3. (color online) Band structure of equilibrium Ni_3C for a large energy range (a) and for a small interval around E_{Fermi} in comparison with 1% uniaxially distorted cells ((b) and (c)). The displayed deformation directions are the ones corresponding to the largest strain (b) and shear (c) components of the relaxed elastic tensor. Bands of positively deformed cells are plotted in red dash-dotted lines, negative deformations in blue dashed lines.

e_1 the in-plane isotropy (xx, yy) is unaffected, while the in-plane/out-of-plane anisotropy changes slightly.

Computational and analytical investigations of the piezoresistivity of semi-conducting CNTs suggest an increase in resistance of well above 50% under longitudinal strains of about 0.3%^{44,45}. To exert the required stress on a Ni_3C -contacted CNT, the contact material would be strained by about 1%, given the ratio of the established Young's modulus of CNTs of about 1000 GPa⁴⁶ and the elastic coefficients we obtained for axial strains in Ni_3C .

This would cause a change in conductivity of 3 to 10% in the contact material, which is significantly smaller than the effect observed in the CNT. Thus, the piezoresistive properties of a device with Ni-contacted CNTs as functional structure are dominated by the electronic response of the CNTs to mechanical deformations.

For isotropic compression of a polycrystalline sample, linear combination of the axial effects suggests a reduction of conductivity. This is mostly a result of the relatively large decrease in conductivity by axial compression in z direction.

The piezoresistive effect observed by Uhlig et al. in Ni_3C -containing nickel-carbon thin films^{1,3} under hydrostatic pressure is opposite to this prediction for bulk Ni_3C based on our calculations. Thus our study excludes the possibility, that these observations are dominated by bulk effects in Ni_3C grains. One may speculate that they emerge from effects in nickel grains, since nickel itself is known to show piezoresistive effects^{47,48}. Effects at interfaces in the nickel-carbon mixture may also play a role.

TABLE III. Relative changes in transport properties of Ni_3C under strain in e_1 (x) and e_3 (z) direction, respectively. Within the accuracy of the calculations, transport coefficients in x and y directions are affected equally by the considered strain values.

strain	$\Delta\varsigma_{xx}/\varsigma_{xx}$	$\Delta\varsigma_{zz}/\varsigma_{zz}$	$\Delta v_x/v_x$	$\Delta v_z/v_z$
$e_1 = +1\%$	-3%	0	-2%	-0.4%
$e_1 = -1\%$	+3%	0	+2%	+0.6%
$e_3 = +1\%$	+4%	+10%	+1%	+4%

IV. CONCLUSIONS

The complete sets of elastic constants of nickel carbides have been calculated in a way that they can be expected to be within 10 GPa of experimental values. The electronic structure and electronic transport properties of bulk Ni_3C under stress have been investigated. Assuming a constant relaxation time τ , changes in conductivity not exceeding about 4% in-plane and about 10% out-of-plane for stresses below 3 GPa are predicted. As

a contact material in sensing applications these changes are of minor significance. These results also show, that Ni_3C does not contribute significantly to the piezoresistive effects observed in nickel-carbon thin films by Uhlig and coworkers¹.

For the formation enthalpy of both Ni_2C variants, the absolute values obtained here differ quantitatively from those by Gibson et al.²¹, but qualitatively both studies agree on the relative ordering with respect to the other carbide phases. On the enthalpy difference between the ground state Ni_2C variants the agreement is excellent. The studies also agree on the formation enthalpies of the other carbides.

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