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Extreme elastic anisotropy of cementite, Fe_3C: First-principles calculations and experimental evidence

M. Nikolussi,[a] S.L. Shang,[b] T. Gressmann,[a] A. Leineweber,[a,*] E.J. Mittemeijer,[a] Y. Wang[b] and Z.-K. Liu[b]

[a] *Max Planck Institute for Metals Research, Heisenbergstrasse 3, D-70569 Stuttgart, Germany*
[b] *Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA*

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First-principles results for the full set of elastic constants (stiffnesses) c_{ij} of cementite, Fe_3C, revealed an extreme elastic anisotropy with a very small c_{44} amounting to only about 1/10 of c_{55} and c_{66}. Synchrotron X-ray diffraction stress measurements were performed on Fe_3C layers grown on α-Fe exhibiting a planar state of compressive residual stress. These data exhibit a characteristic *hkl*-dependence of the stress-induced reflection shifts, and provide experimental proof for the extreme elastic anisotropy of Fe_3C.

Keywords: Fe_3C (cementite); X-ray diffraction (XRD) stress measurements; First-principles calculations; Elastic anisotropy; Residual stresses

Cementite, Fe_3C, is one of the most important phases present in the majority of steels. Notwithstanding the huge number of applications of steels, their properties are far from fully understood, mainly owing to the dearth of fundamental data of Fe_3C. In particular, the full set (nine independent) of single-crystal elastic constants[1] (SECs) of orthorhombic [1–3] Fe_3C has not been reported experimentally. Only partial (experimental) information is available for the SECs of Fe_3C [4–6]. None of these works suggests an extraordinarily large elastic anisotropy. Very recently the full set of nine independent elastic constants of Fe_3C, only at a pressure of 0 atm, was provided by first-principles calculations [7] during the preparation of the present manuscript; an experimental verification was not given.

The present work aims at obtaining a greater insight into the extremely anisotropic elastic properties of Fe_3C. Firstly, the SECs of Fe_3C were calculated by first-principles methods as a function of pressure. Secondly, the observed anisotropy was confirmed experimentally by X-ray diffraction stress measurements on macrostressed, massive, polycrystalline Fe_3C layers grown on α-Fe substrates.

First-principles calculations were performed by the projector-augmented wave method [8] and the generalized gradient approximation [9] as implemented in the VASP code [10] by employing a plane-wave energy cutoff of 500 eV and a reciprocal space *k*-point sampling of $10 \times 7 \times 11$ in the first Brillouin zone. The elastic constants were determined applying the stress vs. strain method with strains of ± 0.007 (see details in Ref. [11]). To this end, for a given strained Fe_3C structure, the atomic arrangement was relaxed; in these calculations reciprocal-space energy integration was performed using the Methfessel–Paxton technique [12]. Afterwards, for that relaxed strained Fe_3C structure, definitive stresses were calculated by reciprocal-space integration using the tetrahedron method incorporating Blöchl corrections [13]. The thus obtained stress–strain relationships were used to calculate the elastic constants of Fe_3C, essentially pertaining to a temperature of 0 K. Due to the magnetic nature of Fe, all the first-principles calculations were performed with the spin polarization approximation.

The calculated stiffnesses c_{ij} of Fe_3C, together with a couple of derived mechanical properties for a quasi-isotropic polycrystalline aggregate, are presented in Table 1 for different unit cell volumes (the theoretically predicted equilibrium unit cell volume is $V_0 = 151.7\ \text{Å}^3$)

* Corresponding author. Tel.: +49 711 689 3365; fax: +49 711 689 3312; e-mail: a.leineweber@mf.mpg.de

[1] The SECs are given in terms of c_{ij} resp. s_{ij} using Voigt matrix notation for the stiffness or compliancy tensors. The constants are defined with respect to a Cartesian coordinate system with the basis axes parallel to [100], [010] and [001]. The latter crystallographic directions refer to a choice of axes with $a = 5.09$ Å, $b = 6.74$ Å, $c = 4.52$ Å [1], i.e. *Pnma* space group setting.

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Table 1. Single-crystal elastic stiffnesses c_{ij} (in GPa) of Fe_3C (*Pnma*) and magnetic moment M (in μ_B) per Fe atom as obtained by first-principles calculations for different values of unit cell volume V (in Å^3) and external pressure p (in GPa) and at 0 K

V	p	M	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{23}	B	G
142.8	15	1.68	459	413	353	25	148	158	216	177	238	276 (272)	106 (67)
151.7[a]	*0*	*1.87*	*385*	*341*	*316*	*13*	*131*	*131*	*157*	*162*	*167*	*224 (223)*	*92 (43)*
156.3	−6	1.93	358	299	285	−3	122	118	131	145	137	196 (195)	83 (−15)
161.0	−11	1.98	305	260	234	−13	112	104	104	108	110	160 (159)	72 (−142)
155.3 [1]	10^{-4}	1.87 [2]										174 [5]	74 [22]

The corresponding bulk modulus B and shear modulus G for textureless polycrystals of Fe_3C according to Voigt and Reuss (in parentheses) for extreme cases of grain interaction are shown in the last two columns. In the last row, available experimental data.

[a] This row corresponds to the theoretically predicted equilibrium unit cell volume ($=V_0$) at zero pressure and at 0 K. The stiffnesses c_{ij} were used for the analyses of the X-ray diffraction stress measurement data. The compliances s_{ij} can be calculated by inversion of the matrix made up by the c_{ij} values. Thus, for V_0 (zero pressure, 0 K): $s_{11} = 0.0035$, $s_{22} = 0.0042$, $s_{33} = 0.0047$, $s_{44} = 0.077$, $s_{55} = 0.0076$, $s_{66} = 0.0076$, $s_{12} = -0.0010$, $s_{13} = -0.0013$, $s_{23} = -0.0017$ (all in GPa^{-1}).

and external pressures. For ambient pressure ($p \approx 0$ GPa) the results comply largely with those of Ref. [7]. Evidently, a relatively extremely small value for the shear modulus c_{44}, amounting to only about 1/10 of c_{55} or c_{66} (at V_0), occurs. This extent of anisotropy may be compared, for example, with the anisotropy ratio of cubic materials, which is basically the ratio of the maximal and minimal shear moduli, $2c_{44}/(c_{11} - c_{12})$. For example, for face-centered cubic-type metals an extreme anisotropy ratio of 7 is found for δ-plutonium [14], implying that in this already extreme case anisotropy occurs that is still smaller than that predicted here for Fe_3C (a factor of 7 for δ-plutonium compared to a factor of 10 for Fe_3C for the ratio of the extreme shear moduli of these materials). The small value of c_{44} of Fe_3C indicates a small shear resistance on (0 0 1) planes in the [0 1 0] direction, corresponding to a change in the orthorhombic lattice angle α away from 90°. The anisotropy manifests itself also in a plot of reciprocal Young's modulus [15], $1/E^{hkl}$, in the (1 0 0) plane; $1/E^{hkl}$ has its maxima approximately along the bisectors of the ⟨0 1 0⟩ and ⟨0 0 1⟩ directions (approximately in [0 2 3] directions; Fig. 1). It must be noted that according to the Born–Huang elastic stability criterion [15] $c_{44} > 0$ must hold. With increasing unit cell volume ($V/V_0 > 1.03$; cf. Table 1), c_{44} even becomes negative, indicating an elastic instability, which could hint at a ferroelastic phase transition [16] or at melting [17]. In reality, such negative values for c_{44} for Fe_3C may be achieved at high temperatures (after thermal expansion) or at artificially applied negative pressures (state of tensile (hydrostatic) stress). However, no observations, hinting at an unusual effect due to a negative c_{44} of Fe_3C, have been reported in the literature.

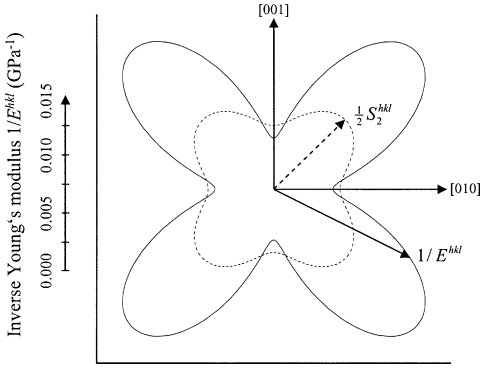

Figure 1. Direction dependence of the inverse Young's modulus $1/E^{hkl}$ (continuous line) and of the XEC $\frac{1}{2}S_2^{hkl} \triangleq \left[\frac{1+\nu}{E}\right]^{hkl}$ (dashed line) in the (1 0 0) plane for [0 *k l*] directions. The high compliances in the bisectors are the effect of the extremely small c_{44} (large s_{44}). For a given direction, $1/E^{hkl}$ is given by the length of an arrow (see scale at left) from the origin to the curve.

The predicted equilibrium volume ($V_0 = 151.7$ Å^3) and lattice parameters a, b and c (5.036, 6.724 and 4.480 Å, respectively), pertaining to 0 K, are somewhat smaller than the values measured at room temperature (155.3 Å^3; 5.09, 6.74 and 4.52 Å [1]). Further, the predicted magnetic moment of 1.87 μ_B per Fe atom (Table 1), indicating that Fe in Fe_3C is in a high spin state, matches the value determined from magnetization measurements [2]. The value predicted for the bulk modulus (224 GPa according to the Voigt approximation [18]) is in good agreement with the previous first-principles results of 212 GPa [19], 229 GPa [20] and 235 GPa [21], and is somewhat larger than the experimental value obtained from the equation-of-state fitting (volume vs. pressure) applied to high-pressure X-ray powder diffraction data (174 GPa [5]). The experimental value for the shear modulus of polycrystalline Fe_3C [22] agrees well with the calculated value (Table 1), considering also the large difference between the values calculated for the two extreme types (Voigt and Reuss) of elastic grain interaction [18]. Further available experimental data concern the anisotropic compressibility [5], as determined from lattice-parameter data at high pressures, and the Young's moduli along the [1 0 0], [0 1 0] and [0 0 1] directions [4].[2] None of the previously obtained experimental partial data on SECs of Fe_3C hint at an extreme elastic anisotropy due to a relatively very small c_{44} value as predicted by first-principles calculations in Ref. [7] and in the present work.

Experimental evidence for the predicted extremely small c_{44} was obtained by X-ray diffraction analysis of (macro)stress in polycrystalline Fe_3C layers grown on α-Fe substrates. The *hkl*-dependent stress-induced shift of peak maxima observed in such measurements provides information on the state of stress, but the data also

[2] In Ref. [7] these somewhat differing Young's moduli have misleadingly been indicated as demonstrating the high elastic anisotropy of Fe_3C. However, the extreme anisotropy of the SECs found here and in [7] originates from the very small value of c_{44}, contributing to the Young's moduli along the metrical directions.