Magnetoelasticity of Fe: Possible failure of *ab initio* electron theory with the local-spin-density approximation and with the generalized-gradient approximation

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The magnetoelastic coupling constant B_2 and the related magnetostriction coefficient λ_{111} of bcc Fe are calculated by the *ab initio* density functional electron theory in local-spin-density approximation and in generalized-gradient approximation. Both B_2 and λ_{111} exhibit a wrong sign as compared to the available experimental data, indicating a possible deficiency of the two approximations for the exchange-correlation functional.

All practical calculations within the framework of the *ab initio* density functional electron theory involve approximations for the exchange-correlation functional of the total energy. The two most frequently used approximations are the local-spin-density approximation[1] (LSDA) where the exchange-correlation energy of the inhomogeneous electron gas is locally approximated by the exchange-correlation energy of the homogeneous electron gas at the respective local electron density,[2] and the generalized-gradient approximation (GGA) (see Ref. 3, and references therein) where the exchange-correlation functional takes into account, in the spirit of a Taylor expansion, not just the local electron density but also its gradient. In spite of the very great success of the LSDA to describe the properties of solids, there are also some deficiencies. One example is the "overbinding" of LSDA, i.e., lattice constants are in general underestimated by a few percent, while cohesive energies and bulk moduli are correspondingly overestimated. The bonding strength is reduced in GGA, and therefore GGA yields improved results for the cohesive properties for systems with a LSDA overbinding. On the other hand, in systems for which the LSDA gives rather accurate results, the GGA may lead to an "underbinding" and hence to a deterioration of the results.[4].

It is of great interest to explore the limitations of LSDA and GGA. The $3d$-metal Fe thereby is a well-known example for a failure of LSDA which predicts that nonmagnetic fcc Fe is energetically slightly more favorable than ferromagnetic bcc Fe, in contrast to the experimental observations, whereas GGA yields the correct ferromagnetic bcc ground state structure (see Ref. 5, and references therein). In the present paper we show, however, that the GGA does not describe all the ground-state properties of bcc Fe correctly: both LSDA and GGA yield the wrong sign for the magnetoelastic coupling constant B_2 and the related magnetostrictive coefficient λ_{111} as compared to the experimental data.

The calculation of the magnetoelastic properties of metals has been considered as a big challenge for the *ab initio* electron theory. In 1993 it has been stated[6] that "even with to-day's supercomputers, precision is insufficient for an *ab initio* band-structure calculation of magnetostriction." In the meanwhile, improved calculational methods and computer efficiencies made an *ab initio* treatment of magnetoelasticity in rare-earth[7] metals and in transition metals[8–15] feasible. The results for the magnetoelastic coupling coefficient B_1 and the related magnetostriction coefficient λ_{001} of bcc Fe, fcc Co, and fcc Ni obtained by GGA agreed[12,15] rather well with experimental data when a full-potential band structure method was used. In most cases, the LSDA results were less accurate,[12,15] especially for Fe where λ_{001} and B_1 were overestimated by a factor between 2 and 3, respectively. The *ab initio* calculations[15] were even able to provide data on some of the nonlinear magnetoelastic coupling coefficients for bcc Fe, fcc Co, and fcc Ni. It was shown experimentally[16–19] and theoretically[13–15] that the magnetoelastic properties of thin films with large epitaxial strains are different from those of weakly strained bulk materials if the results are interpreted by a first-order magnetoelastic theory with effective first-order magnetoelastic coupling constants. For instance, for experiments which in the case of small strains would involve only the first-order constant B_1 [see Eq. (1)], one has to introduce effective constants which depend linearly on the epitaxial strain ϵ_0. It was suggested[16–19] that nonlinear magnetoelastic effects are responsible for this difference. By means of the phenomenological nonlinear magnetoelastic theory, based on the symmetrized strain variables,[6] it could be shown[20] that different effective coupling constants $B_1^{\text{eff}} = B_1 + D^{\text{eff}}\epsilon_0$ and $\tilde{B}_1^{\text{eff}} = B_1 + \tilde{D}^{\text{eff}}\epsilon_0$ have to be used for the interpretation of the magnetostrictive stress experiments[17–19] and for the measurements of the strain-induced magnetic anisotropy energy, and D^{eff} as well as $\tilde{D}^{\text{eff}}$ could be related to some of the second-order magnetoelastic coupling constants appearing in this phenomenological theory. By a combination of the *ab initio* electron theory with the phenomenological magnetoelastic theory these second-order coupling constants could be calculated.[15] For D^{eff} the same order of

magnitude was found as in the experiment, confirming the abovementioned suggestion. Similarly, it has been shown[21] for the case of epitaxial Fe films that for the interpretation of magnetostrictive stress experiments for a geometry which for the case of small strains would involve only the first-order coupling constant B_2 [see Eq. (1)], an effective constant B_2^{eff} has to be introduced that again depends linearly on the large epitaxial strains ϵ_0. First theoretical hints for a strain dependence of the effective coupling constant $\widetilde{B}_2^{\mathrm{eff}}$ for the strain-induced magnetic anisotropy energy were found by the *ab initio* calculation of Guo[14] for fcc Co and fcc Ni. In Ref 22, the relation between the strain dependence of B_2^{eff} and some of the second-order magnetoelastic coupling constants of the symmetrized phenomenological nonlinear magnetoelastic theory was found, and the first-order constant B_2 as well as these nonlinear constants were calculated *ab initio* for bcc Fe, fcc Co, and fcc Ni. Thereby, the most striking results were found for B_2. For Co and Ni, the GGA results agreed rather well with the experimental data. The LSDA results for the materials were worse but at least of the same order of magnitude and of the correct sign. In contrast, for bcc Fe both the LSDA result (-7 MJ/m^3) and the GGA result (-3.9 MJ/m^3) had another sign than the experimental result[21] (7.62 MJ/m^3). Because this indicates a serious deficiency both of LSDA and GGA for the calculation of the magnetoelastic properties of Fe, we have now re-examined this striking result by various calculational methods and by the use of different band-structure methods.

In the following we use three different types of calculational methods. The first two determine B_2 from the strain-induced magnetoelastic contribution e_{MCA} to the magnetocrystalline anisotropy energy density, and the third one determines the magnetostriction coefficient λ_{111} from the strain-derivative of e_{MCA}. The quantity λ_{111} is related to B_2 via $B_2 = -3 C_{44} \lambda_{111}$ with the elastic constant C_{44}.

The calculation 1 starts from the first-order expression for the strain-induced magnetoelastic contribution $e_{\mathrm{me}}^{(1)}$ to the magnetocrystalline anisotropy energy density of a cubic material:

$$e_{\mathrm{me}}^{(1)} = B_1(\epsilon_{11}\alpha_1^2 + \epsilon_{22}\alpha_2^2 + \epsilon_{33}\alpha_3^2)$$
$$+ 2B_2(\epsilon_{12}\alpha_1\alpha_2 + \epsilon_{23}\alpha_2\alpha_3 + \epsilon_{31}\alpha_3\alpha_1), \quad (1)$$

where the ϵ_{ij} are the components of the strain tensor and the α_i are the direction cosines describing the orientation of the magnetization. The basic idea is to calculate the strain-induced magnetocrystalline anisotropy energy density e_{MCA}, i.e., the difference in $e_{\mathrm{me}}^{(1)}$ for different magnetization directions in a crystal which is suitably deformed. There are various possible choices of strain modes and magnetization directions for which e_{MCA} depends only on B_2 but not on B_1. In calculation 1 we select the strain modes roughly according to the epitaxial strains which appear in a magnetic film that is grown on a substrate in [110] or [111] orientation.[13,14] We thereby assume a constant volume mode, i.e., we prescribe a lateral strain ϵ_0 and a perpendicular strain in a such a way that the unit cell volume of the unstrained bcc Fe is conserved. As stated above, there are many possible variants of
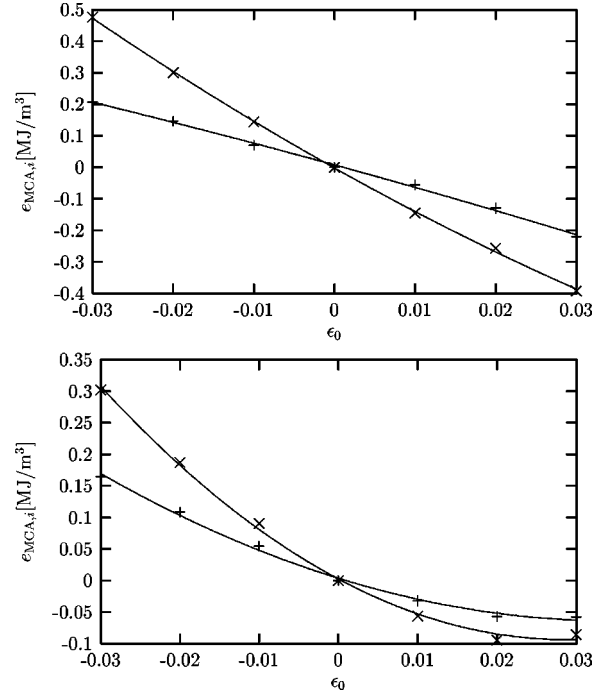

FIG. 1. The *ab initio* data for $e_{\mathrm{MCA,1}}(\epsilon_0)(+)$ and $e_{\mathrm{MCA,2}}(\epsilon_0)$ ($\times$) for LSDA (top) and GGA (bottom), together with the parabolic fits, according to calculation 2.

strain modes for the bulk which are appropriate for a determination of B_2, and this selected strain mode is just one possible variant (another choice is used for calculational method 2). The fact that the strains in real epitaxial films are probably more complicated therefore does not matter at all. For the [110] orientation we then calculate *ab initio* $e_{\mathrm{MCA}} = e(\alpha_1 = -\alpha_2 = \frac{1}{2}\sqrt{2}, \epsilon_0) - e(\alpha_1 = \alpha_2 = \frac{1}{2}\sqrt{2}, \epsilon_0)$ and the quantity $\widetilde{B}_2^{\mathrm{eff}}(\epsilon_0) = -e_{\mathrm{MCA}}/2\epsilon_{12}$ with $\epsilon_{12} = -3\epsilon_0$. For the [111] orientation we calculate *ab initio* $e_{\mathrm{MCA}}(\epsilon_0) = e(\alpha_1 = \alpha_2 = 1/\sqrt{6}, \alpha_3 = -2/\sqrt{6}, \epsilon_0) - e(\alpha_1 = \alpha_2 = \alpha_3 = 1/\sqrt{3}, \epsilon_0)$ and the quantity $\widetilde{B}_2^{\mathrm{eff}}(\epsilon_0) = -e_{\mathrm{MCA}}/3\epsilon_{12}$ with $\epsilon_{12} = -2\epsilon_0$. According to Eq. (1) the first-order constant B_2 may be obtained from extrapolating $\widetilde{B}_2^{\mathrm{eff}}(\epsilon_0)$ to $\epsilon_0 = 0$, and the quantities $-2\epsilon_{12}\widetilde{B}_2^{\mathrm{eff}}(\epsilon_0)$ and $-3\epsilon_{12}\widetilde{B}_2^{\mathrm{eff}}(\epsilon_0)$ are the strain-induced magnetic anisotropies for [110] and [111] orientation, respectively, at large strains ϵ_0 for which non-linear magnetoelastic effects became essential.

Calculation 2 is more evolved. Instead of using the first-order expression $e_{\mathrm{MCA}}^{(1)}$ for the magnetoelastic energy density given by Eq. (1) it is based on the phenomenological expression for the magnetoelastic energy density containing first- and second-order terms of symmetrized strain variables.[6] We calculate by the *ab initio* electron theory the strain-induced magnetocrystalline anisotropy energies for two differently strained crystals, namely $e_{\mathrm{MCA,1}} = e(\epsilon_{11} = \epsilon_{12} = \epsilon_0, \alpha_1 = \alpha_2 = \frac{1}{2}\sqrt{2}) - e(\epsilon_{11} = \epsilon_{12} = \epsilon_0, \alpha_2 = 1)$ and $e_{\mathrm{MCA,2}} = e(\epsilon_{33} = \epsilon_{12} = \epsilon_0, \alpha_1 = \alpha_2 = \frac{1}{2}\sqrt{2}) - e(\epsilon_{33} = \epsilon_{12} = \epsilon_0, \alpha_2 = 1)$, and we represent the data points by parabola, $e_{\mathrm{MCA,1}} = a_1\epsilon_0 + b_1\epsilon_0^2$ and $e_{\mathrm{MCA,2}} = a_2\epsilon_0 + b_2\epsilon_0^2$, see Fig. 1, assuming that the strain-independent contribution to the magnetocrystalline anisot-

ropy energy density is negligible. By the phenomenological second-order magnetoelastic theory it can be shown (for details see Ref. 22) that the coefficients a_1, b_1, a_2, and b_2 may be expressed as linear combination of B_2 and two second-order magnetoelastic coupling constants (as well as B_1 and two other second-order constants which determine B_1^{eff} and which have already been calculated in Ref. 15). From the coefficients a_1, b_1, a_2, and b_2 fitted to the *ab initio* data we therefore can determine not only B_2 but also the two additional second-order constants, and this is an advantage over the calculational method 1.

Calculation 3 starts from the linearized theory of magnetostriction of a cubic material, which yields the following

expression for the magnetostrictive change Δl in length along $(\beta_1, \beta_2, \beta_3)$ when magnetizing the sample in the direction $(\alpha_1, \alpha_2, \alpha_3)$ with respect to the crystalline axes:

$$\frac{\Delta l}{l_0} = \frac{3}{2}\lambda_{001}\left(\sum_{i=1}^{3}\alpha_i^2\beta_i^2 - \frac{1}{3}\right) + 3\lambda_{111}(\alpha_1\alpha_2\beta_1\beta_2$$
$$+ \alpha_2\alpha_3\beta_2\beta_3 + \alpha_3\alpha_1\beta_3\beta_1), \tag{2}$$

where l_0 denotes the corresponding length in the nonmagnetized state. The magnetostriction coefficient λ_{111} thus may be obtained by measuring the fractional change in length along the [111] direction ($\beta_i = 1/\sqrt{3}$) when switching the magnetization direction from [111] to [11$\bar{2}$]:

$$\lambda_{111} = -\frac{2}{3}\frac{l_0\left(\alpha_1 = \alpha_2 = \frac{1}{\sqrt{6}}, \alpha_3 = -\frac{2}{\sqrt{6}}\right) - l_0\left(\alpha_1 = \alpha_2 = \alpha_3 = \frac{1}{\sqrt{3}}\right)}{l_0\left(\alpha_1 = \alpha_2 = \alpha_3 = \frac{1}{\sqrt{3}}\right)}, \tag{3}$$

where it is assumed that $\lambda_{111} \ll 1$. In principle λ_{111} could be determined from the equilibrium lengths $l_0(\alpha_1 = \alpha_2 = 1/\sqrt{6}, \alpha_3 = -2/\sqrt{6})$ and $l_0(\alpha_1 = \alpha_2 = \alpha_3 = 1/\sqrt{3})$ of the unit cell along the [111] axis for the two orientations of the magnetization obtained by minimization of the total energy, which, however, would be numerically rather delicate. Instead we proceed on the line of Wu *et al.*[12]: We calculate the total energy density $e(\alpha_1 = \alpha_2 = \alpha_3 = 1/\sqrt{3}, l)$ as a function of length l for a constant-volume mode and fit the *ab initio* data by a parabola, $al^2 + bl + c$, see Fig. 2, yielding $l_0(\alpha_1 = \alpha_2 = \alpha_3 = 1/\sqrt{3}) = -b/2a$. Furthermore, the magnetocrystalline anisotropy energy density $e_{\text{MCA}}(l) = e(\alpha_1 = \alpha_2 = 1/\sqrt{6}, \alpha_3 = -2/\sqrt{6}, l) - e(\alpha_1 = \alpha_2 = \alpha_3 = 1/\sqrt{3}, l)$ is calculated as a function of l, Fig. 2, and then $l_0(\alpha_1 = \alpha_2$

FIG. 2. The total energy $e(\alpha_1 = \alpha_2 = \alpha_3 = 1/\sqrt{3}, l)$ per unit cell as function of the length l along the [111] direction, and the magnetocrystalline anisotropy energy per unit cell $e_{\text{MCA}}(l)$ according to calculation 3.

$= 1/\sqrt{6}, \alpha_3 = -2/\sqrt{6}$) is obtained from $-b/2a - 1/2a \, \partial e_{\text{MCA}}/\partial l|_{l_0}$. From Eq. (3) we finally find $\lambda_{111} = -2/3b \, \partial e_{\text{MCA}}/\partial l|_{l_0}$. It becomes obvious from Fig. 2 that e_{MCA} exhibits a strong nonlinear trend. A third order polynomial fit is required to represent the data in the whole range of considered l/l_0 values. This means that for pure shear-strain distortions of Fe the influence of third-order magnetoelastic constants becomes relevant for strains which are accessible in epitaxial films. (In our preliminary calculation for Co and Ni we did not find this peculiarity.) The quantity $\partial e_{\text{MCA}}/\partial l|_{l_0}$ is obtained from the linear term of the polynomial fit.

For calculation 1 the spin-polarized relativistic (SPR) linear muffin-tin-orbital method[23] (LMTO) was applied which adopts the atomic-sphere approximation[24,25] (ASA) for the effective potential, with s, p and d muffin-tin orbitals and with the combined-correction terms.[24,25] We used the Vosko-Wilk-Nusair parametrization[26] for the LSDA and the GGA functional of Perdew *et al.*[27] The anisotropy energy e_{MCA} was calculated by means of the force theorem.[28] For calculation 2 we applied the WIEN97 code[29] which adopts the full-potential linearized-augmented-plane-wave method (FLAPW) not involving any shape approximations for the potential. We used the LSDA functional of Perdew and Wang[30] and the GGA functional of Perdew *et al.*[3] The anisotropy energy e_{MCA} was again calculated by means of the force theorem, and spin-orbit coupling was treated perturbatively using the second variational method.[31] For calculation 3 we used the Northwestern FLAPW code[32] and the GGA functional of Perdew *et al.*[3] The energy density e_{MCA} was calculated by the torque method,[33] and the spin-orbit coupling was treated by the second variational method. In all calculations a satisfactory convergence with respect to the convergence parameters of the band-structure method was
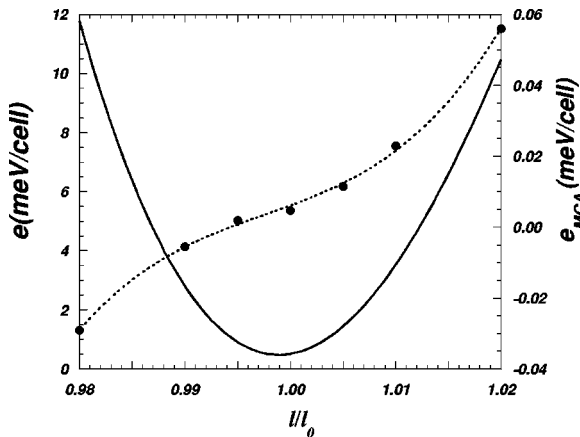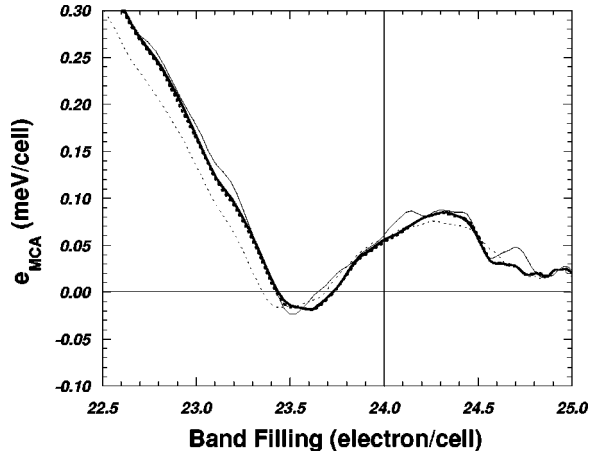
FIG. 3. The magnetocrystalline anisotropy energy density e_{MCA} of calculation 3 versus the filling of the d band for $l/l_0=1.02$ with different number of $\mathbf{k}$ points ($N_{\mathbf{k}}$) and basis energy cutoffs (E_{cut}). Thick solid line: $N_{\mathbf{k}}=13\,858$ and $E_{cut}=16$ Ry; thick dashed line: $N_{\mathbf{k}}=13\,858$ and $E_{cut}=20.25$ Ry; thin solid line: $N_{\mathbf{k}}=4626$ and $E_{cut}=16$ Ry; thin dotted line: $N_{\mathbf{k}}=13\,858$ and $E_{cut}=12.25$ Ry.

TABLE I. Results for B_2 (in MJ/m^3) from the three types of calculations. For calculation 3, B_2 was obtained from $B_2=-3C_{44}\lambda_{111}$ with the value $\lambda_{111}=12\times10^{-6}$ calculated by GGA and with the experimental value $C_{44}=1.15\times10^{11}$N/m^2. The experimental results are $B_2=+7.62$ MJ/m^3, see Ref. 21, and $\lambda_{111}=-22.7\times10^{-6}$, see Ref. 19.

	1	2	3
LSDA	−1.84	−7.0	
GGA	−4.04	−3.9	−4.14

Table I gives the results for B_2 from the three types of the calculations. It becomes clear that all three calculations yield another sign of B_2 than the experiment, both for LSDA and GGA.

There are two possible conclusions. First, the results may indicate a deficiency of the two most frequently used approximations LSDA and GGA for the exchange-correlation functional of the *ab initio* density functional electron theory for the calculation of the magnetoelastic properties of Fe. Second, one could also suspect that there are problems with the former experimental determinations of λ_{111} and B_2 for Fe. For instance, to obtain single-crystalline Fe, the materials were doped with Si atoms in the past and this may reduce the average d-occupation number. It becomes obvious from Fig. 3 that there is a range of reduced d-band filling for which a change in sign for λ_{111} and B_2 is expected. We therefore suggest that the experimental determination of λ_{111} and B_2 is repeated for the nowadays available ultrapure Fe single crystals.

obtained. As an example, Fig. 3 shows $e_{MCA}(l)$ of calculation 3 for $l/l_0=1.02$ as a function of the band filling for different energy cutoffs for the basis set of the FLAPW method and for different numbers of $\mathbf{k}$ points used for the sampling of the Brillouin zone. A cutoff of 16 Ry is obviously sufficient, since a 20.25 Ry cutoff gives almost identical e_{MCA} in the whole range of band filling. In contrast, a 12.25 Ry cutoff is too small and its use causes an obvious shift of the e_{MCA} curve. A number of 13 858 $\mathbf{k}$ points for the sampling of the irreducible Brillouin zone also appears to be large enough since the results with 4626 $\mathbf{k}$ points are already reasonably close. Finally, an energy cutoff of 225 Ry was used for the representation of the charge density and the potential.

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