First-principles calculations of the spontaneous volume magnetostriction based on the magnetoelastic energy

P. Nieves1, S. Arapan1, and D. Legut1
1 IT4Innovations, VŠB - Technical University of Ostrava, 17. listopadu 2172/15, 70800 Ostrava-Poruba, Czech Republic
(Dated: July 8, 2022)

We present a simple methodology to compute the spontaneous volume magnetostriction with first-principles calculations on the basis of the magnetoelastic energy. This method makes use of deformations of the unit cell only at the ferromagnetic state. Hence, it does not require the difficult first-principles calculation of the equilibrium volume at the paramagnetic state. To validate this methodology, we apply it to body-centered cubic Fe and face-centered cubic Ni single crystals, finding consistent results with experiment and previous first-principles calculations. The simplicity and reliability of this approach could be exploited in the high-throughput screening of spontaneous volume magnetostriction, as well as associated quantities like isotropic magnetoelastic constants and isotropic magnetostrictive coefficients.

I. INTRODUCTION

The spontaneous volume magnetostriction (ωv) is a fundamental property of magnetic materials responsible for interesting features like anomalies in the thermal expansion coefficient. It is defined as the fractional volume change between magnetically ordered and paramagnetic state, and is mainly originated by the volume dependence of both atomic magnetic moments and exchange interaction. Other less significant contributions to ωv are the isotropic contribution of the dipolar magnetostriction (form effect) and crystal effect. The experimental and theoretical study of ωv is not straightforward due to the difficulties in the characterization of the equilibrium volume at hypothetic paramagnetic-like state below the Curie or Neél temperature. In experiment, such equilibrium volume is typically estimated by an extrapolation using the Debye theory and the Grüneisen relation. On the other hand, the paramagnetic state at zero-temperature can be studied with first-principles calculations through the Stoner model, disordered local moment (DLM) approach and special-quasirandom structures (SQS). For example, first principles calculations of ωv showed that the Stoner model might overestimate it in body-centered cubic (bcc) Fe while a better quantitative agreement with experiment is achieved through the disordered local moment (DLM) approach.

In practice, despite the theoretical description of the paramagnetic state at zero-temperature is double, the calculation of ωv using the paramagnetic state is still a tedious task. So in this sense, it would be desirable to find alternative ways to compute ωv which could be easily automated, making it more suitable for high-throughput screening. In this work, we explore a new theoretical approach to compute ωv at zero-temperature through Density Functional Theory (DFT) calculations which does not require the difficult direct evaluation of the equilibrium volume at the paramagnetic state. This method is derived directly from the isotropic part of the magnetoelastic energy via the theoretical relationship between the isotropic magnetoelastic constant and ωv.

II. METHODOLOGY

Let us start by introducing some basic concepts of the theory of magnetoelasticity. The magnetoelastic energy density (energy per volume) of cubic crystals (point groups 432, 43m, m3m) is typically written as

\[ E_{me} = b_0(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) + b_1(\alpha_x^2\varepsilon_{xx} + \alpha_y^2\varepsilon_{yy} + \alpha_z^2\varepsilon_{zz}) \]

+ \[ 2b_2(\alpha_x\alpha_y\varepsilon_{xy} + \alpha_y\alpha_z\varepsilon_{yz} + \alpha_z\alpha_x\varepsilon_{zx}) \]

(1)

where \( b_i \) (\( i = 0, 1, 2 \)) are the magnetoelastic constants, \( \varepsilon_{ij} \) is the strain tensor and \( \omega_i \) (\( i = x, y, z \)) are direction cosines of the magnetization. Here, it is convenient to rewrite Eq.1 in the following form:

\[ E_{me} = \frac{1}{3} B^{a,2}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \]

+ \[ B^{b,2}\left(\left[\alpha_x^2 - \frac{1}{3}\right]\varepsilon_{xx} + \left[\alpha_y^2 - \frac{1}{3}\right]\varepsilon_{yy} + \left[\alpha_z^2 - \frac{1}{3}\right]\varepsilon_{zz}\right) \]

+ \[ 2B^{c,2}(\alpha_x\alpha_y\varepsilon_{xy} + \alpha_y\alpha_z\varepsilon_{yz} + \alpha_z\alpha_x\varepsilon_{zx}) \]

(2)

where

\[ B^{a,2} = 3b_0 + b_1, \quad B^{b,2} = b_1, \quad B^{c,2} = b_2. \]

(3)

The definition of the magnetoelastic constants in Eq.2 has the advantage that fully decouples the isotropic and anisotropic magnetic interactions like SOC and crystal field interactions. In the present work, we will exploit this fact since we are interested in the calculation of \( \omega_v \) which mainly arises from isotropic interaction. On the other hand, the elastic energy density for cubic crystals reads:

\[ E_{el} = \frac{C_{11}}{2}(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + C_{12}(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{xx}\varepsilon_{zz} + \varepsilon_{yy}\varepsilon_{zz}) \]

+ \[ 2C_{44}(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2) \]

(4)
where $C_{11}$, $C_{12}$ and $C_{44}$ are the elastic constants. Let us define $l_0$ and $\ell$ as the material lengths along the direction $\mathbf{B}$ when the system is at the paramagnetic and ferromagnetic states, respectively. The fractional change in length $(\ell - l_0)/l_0$ can be obtained from the minimization of the elastic and magnetoelastic energies with respect to the strain tensor within the infinitesimal strain theory, see Refs.\textsuperscript{[10,11]} Under this deformation, the total energy density in Eq.\textsuperscript{[10]} is reduced to

$$E(s) = (C_{11} + C_{12})s^2 + \frac{2}{3}B^{\alpha,2}s + E_0.$$  \hspace{1cm} (12)

Hence, $B^{\alpha,2}$ can be easily obtained by fitting the computed energy with a spin-polarized DFT calculation (without SOC) of the energy. We consider the conventional cubic unit cell of bcc Fe \textsuperscript{[18]}, and assuming the elastic constants are also calculated, then $\omega_\alpha$ is immediately obtained using Eq.\textsuperscript{[18]}

III. RESULTS

Let us now apply this method to compute $\omega_\alpha$ for bcc Fe and fcc Ni at zero-temperature. To this end, we use the Vienna Ab initio Simulation Package (VASP)\textsuperscript{[19]} to perform the spin-polarized DFT calculation (without SOC) of the energy. We consider the conventional cubic unit cell of bcc Fe (2 atoms/cell) and fcc Ni (4 atoms/cell). The interactions were described by the projector augmented wave (PAW) method\textsuperscript{[18]} with 14 valence electrons for bcc Fe and 16 valence electrons for fcc Ni, where we use the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) for the type of exchange-correlation\textsuperscript{[18]} The plane waves basis was generated for an energy cut-off of 586.476 eV for bcc Fe and 735.972 eV for fcc Ni (two times larger than the default value). The energy convergence criterion of the electronic self-consistency was chosen as $10^{-7}$ eV/cell. Firstly, we calculate the equilibrium volume at the ferromagnetic state ($V_{FM}$) by fitting the computed energy for different unit cell volume to the Vinet equation of state (EOS)\textsuperscript{[18]} In
Fig. 1. Calculated equilibrium volume as a function of the smallest allowed spacing between k-points (∆k) in the mesh of the Brillouin zone (input parameter called KSPACING in VASP) for (top) bcc Fe and (bottom) fcc Ni. The equilibrium volume at the ferromagnetic state (\(V_{FM}\)) is obtained by fitting the computed energy for different unit cell volume to the Vinet EOS. Red dash line stands for the averaged equilibrium volume \(\langle V_{FM}\rangle\) considering the data with \(\Delta k \leq 0.125\) Å\(^{-1}\) and \(\Delta k \leq 0.09\) Å\(^{-1}\) for bcc Fe and fcc Ni, respectively.

Fig. 2. Fitting procedure to extract \(B_0^{\alpha,2}\) for (top) bcc Fe and (bottom) fcc Ni. The unit cell with lattice parameter \(a_0 = 2.8309906\) Å (\(V_{FM} = 11.344498\) Å\(^3\)/atom) for bcc Fe and \(a_0 = 3.520486\) Å (\(V_{FM} = 10.90803\) Å\(^3\)/atom) for fcc Ni is deformed according to the parameterized strain tensor \(\varepsilon(s)\) given by Eq. 11. Blue circles give the DFT data, while the red solid line shows the fitting to a quadratic polynomial Eq. 13.

Next, we illustrate the fitting procedure to extract \(B_0^{\alpha,2}\) for Fig. 2. Here, we applied the strain tensor given by Eq. 11 to the conventional unit cell of bcc Fe and fcc Ni with the previously calculated equilibrium volume (\(V_{FM}^{Fe} = 11.344498\) Å\(^3\)/atom and \(V_{FM}^{Ni} = 10.90803\) Å\(^3\)/atom). In this calculation, we used a small spacing between k-points (\(\Delta k = 0.06\) Å\(^{-1}\)). From the quadratic fitting (Eq. 13) of the energy versus strain (free parameter \(s\)) data, we obtain \(B_0^{\alpha,2} = -0.232\) GPa for bcc Fe and \(B_0^{\alpha,2} = -0.135\) GPa for fcc Ni. Similarly, using the same lattice parameter and VASP settings in the program AELAS, we get the following elastic constants: \(C_{11}^{Fe} = 274.3\) GPa, \(C_{12}^{Fe} = 150.8\) GPa, \(C_{44}^{Fe} = 101.4\) GPa, \(C_{11}^{Ni} = 275.9\) GPa, \(C_{12}^{Ni} = 157.5\) GPa, \(C_{44}^{Ni} = 132.2\) GPa which are in reasonable good agreement with experiment. Using the previously calculated elastic constants (\(C_{11}^{Fe} = 243.1\) GPa, \(C_{12}^{Fe} = 138.1\) GPa, \(C_{44}^{Fe} = 121.9\) GPa, \(C_{11}^{Ni} = 261\) GPa, \(C_{12}^{Ni} = 151\) GPa and \(C_{44}^{Ni} = 132\) GPa) and previous DFT calculations, we insert our calculated elastic and magnetoelastic constants in Eq. 13 to obtain the following values for \(\omega_\alpha = 4 \times 10^{-4}\) for bcc Fe and \(\omega_\alpha = 2.3 \times 10^{-4}\) for fcc Ni. In the case of bcc Fe, this result is the same as the experimental value measured by Richter and Lotter: \(\omega_\alpha = (4 \pm 0.4) \times 10^{-4}\), but smaller than those reported by Ridley and Stuart: \(\omega_\alpha = 3.3 \times 10^{-3}\) and \(\omega_\alpha = 7.5 \times 10^{-3}\). A theoretical value about \(\omega_\alpha \sim 10^{-3}\) was calculated by Khmelevskiy.
and Mohn using first-principles calculations with the DLM\textsuperscript{[21]} while higher values ($\omega_0 > 10^{-2}$) have been reported within the Stoner model\textsuperscript{[36]} On the other hand, the obtained value for fcc Ni is close to the experimental value found by Williams\textsuperscript{[59]} $\omega_s = (3.24 \pm 0.15) \times 10^{-4}$ and the theoretical result calculated by Shimizu\textsuperscript{[6]} $\omega_0 = 3.75 \times 10^{-4}$ using the Stoner model. Larger theoretical values than these ones have been also reported ($\omega_0 > 10^{-3}$)\textsuperscript{[51,51]} We point out that negative values of $\omega_0$ have been empirically found for fcc Ni\textsuperscript{[56,59]} which could be related to the extrapolation procedure to estimate $\omega_0$ below $T_0$. The presented methodology can also allow to obtain the equilibrium volume at the paramagnetic state $V_{FM}$ easily by inserting the calculated values of $V_{FM}$ and $\omega_0$ in Eq\textsuperscript{[4]} Similarly, one can get the isotropic magnetostrictive coefficient $\lambda^0$ using the expression $\lambda^0 = \lambda_{a,2}/3 \approx \omega_s/3$. By doing so we find the equilibrium volume $V_{FM}^{Fe} = 11.339962 \, \text{Å}^3/$atom and $V_{FM}^{Ni} = 10.905536 \, \text{Å}^3/$atom. For the isotropic magnetostrictive coefficient we get $\lambda_{a,2}^{Fe} = 133 \times 10^{-6}$ and $\lambda_{a,2}^{Ni} = 77 \times 10^{-6}$ which is one order of magnitude larger than the anisotropic ones in the case of bcc Fe\textsuperscript{[33]} ($\lambda_{001}^{Fe} = 26 \times 10^{-6}$ and $\lambda_{111}^{Fe} = -30 \times 10^{-6}$) and the same order of magnitude than the anisotropic ones in the case of fcc Ni\textsuperscript{[33]} ($\lambda_{001}^{Ni} = -60 \times 10^{-6}$ and $\lambda_{111}^{Ni} = -35 \times 10^{-6}$).

We note that the calculation of $B_{a,2}^{\omega}$ and $\omega_0$ with this procedure is very sensitive to the lattice parameter $a_0$ (volume $V_{FM}$) of the unit cell. This fact is shown in Figs.\textsuperscript{[3]} and \textsuperscript{[4]} where a linear dependence on $V_{FM}$ is observed. Here, we also verified that $\omega_0$ is well converged with respect to $\Delta k$, see inset of Fig.\textsuperscript{[4]}. We see that $\omega_0$ becomes negative at $V_{FM} > 11.35 \, \text{Å}^3/$atom and $V_{FM} > 10.91 \, \text{Å}^3/$atom for bcc Fe and fcc Ni, respectively. This result is associated to the spatial dependence of the exchange interaction $J(r)$\textsuperscript{[21,13,15]} and atomic magnetic moment $\mu$ (important in itinerant ferromagnets)\textsuperscript{[34]}. For example, in localized classical spin-lattice simulations within the Néel model up first nearest neighbors, it turns out that $\omega_0$ is proportional to the derivative of exchange constant $J(r)$ with respect to the interatomic distance $r$ in cubic crystals ($\omega_0 \propto dJ/dr|_{r=0}$). At phenomenological level, it was found that $\omega_0 = \zeta K r^2$, where $K$ is the compressibility and $\zeta$ is the magnetoelastic-coupling constant\textsuperscript{[3]} We also checked that using other strain tensors different from the one given in Eq\textsuperscript{[11]} leads to the same values of $B_{a,2}^{\omega}$ and $\omega_0$. This fact confirms that the strain dependence of the total spin-polarized energy without SOC is well described by Eq\textsuperscript{[10]} for bcc Fe and fcc Ni under small deformations.

![FIG. 3. Calculated isotropic magnetoelastic constant $B_{a,2}^{\omega}$ and elastic constants $C_{ij}$ for (top) bcc Fe and (bottom) fcc Ni using different volume of the unit cell.](image)

![FIG. 4. Calculated spontaneous volume magnetostriction $\omega_0$ for (top) bcc Fe and (bottom) fcc Ni using different volume of the unit cell. Vertical dash orange line shows the equilibrium volume $<V_{FM}>$ obtained in Fig\textsuperscript{[4]} Inset shows the analysis of the convergence of $\omega_0$ with respect to the smallest allowed spacing between k-points ($\Delta k$) in the mesh of the Brillouin zone for the case $<V_{FM}>$.](image)
Lastly, it is worth mentioning a possible inconsistency related to $\omega_i$ in classical spin-lattice models. Typically, in these models a classical interatomic potential is combined with a Heisenberg spin Hamiltonian in order to couple lattice and spin dynamics. Unfortunately, this strategy sometimes leads to an unphysical situation, where at the state with the minimum energy (at zero-temperature) the pressure is not exactly zero. To overcome this problem, an offset in the exchange energy is frequently used.

$$E_{ex} = -\frac{1}{2} \sum_{i=1}^{N} J(r_{ij})(\mathbf{s}_i \cdot \mathbf{s}_j - 1),$$

(15)

where $N$ is the total number of atoms in the system, $r_{ij}$ is the distance between atom $i$ and $j$, and $\mathbf{s}_i$ is the normalized atomic magnetic moment vector of atom $i$. We note that this offset in the exchange energy can lead to different values of $\omega_i$ with Eqs.7 and 8 using a classical spin-lattice model. The reason for that is because this offset set the exchange energy to zero for any lattice parameter of the ferromagnetic state at zero temperature (collinear spin state $\mathbf{s}_i \parallel \mathbf{s}_j \forall i, j$), modifying the isotropic magnetoelastic constant $B^{\alpha,2}$ artificially. Consequently, the method described in Section II will lead to inconsistent results for $\omega_i$ if such offset is included in the spin-lattice model. We verified that removing this offset in the spin-lattice models described in Refs.5 gives the same value for $\omega_i$ with Eqs.7 and 8 which also validates the methodology described in Section II.

IV. CONCLUSIONS

In summary, the presented methodology based on the magnetoelastic energy provides a simple, fast and reliable approach to compute $\omega_i$. One of the main advantage of this method is that does not require the tedious calculation of the equilibrium volume at the paramagnetic state. This fact greatly facilitates its implementation for massive calculations of $\omega_i$ and associated quantities (like $B^{\alpha,2}$ and $\lambda^\alpha$) in a high-throughput way.

We illustrated this new concept by applying it to bcc Fe and fcc Ni, finding a reasonable good agreement with experiment and theory. We showed that the results depends strongly on the lattice parameter, so that it is convenient to obtain the equilibrium lattice parameter accurately before computing $\omega_i$. Additionally, we further validated the presented methodology using classical spin-lattice models, where we found that the offset in the exchange energy should not be included in order to get consistent results between the fractional change in volume (Eq.7) and magnetoelastic energy (Eq.8).

Presently, we are working on a new version of the program MAELAS, where we plan to include this method for cubic crystals, as well as for lower crystal symmetries.

ACKNOWLEDGEMENT

This work was supported by the ERDF in the IT4Innovations national supercomputing center - path to exascale project (CZ.02.1.01/0.0/0.0/16-013/0001791) within the OPRDE and projects “e-INFRA CZ (ID:90140)” and Donau No. 8X20050 by The Ministry of Education, Youth and Sports of the Czech Republic. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 863155.
