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# First principles study on the magnetocrystalline anisotropy of Fe–Ga magnetostrictive alloys*

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This paper investigates the electronic structure and magnetocrystalline anisotropy of Fe–Ga magnetostrictive material by means of the full potential-linearized augmented plane-wave method within the generalized gradient approximation. The 3d-orbit splitting of Fe atoms in $D0_3$, B2-like and $L1_2$ crystalline structures of Fe–Ga is calculated with consideration of the crystal field as well as the spin–orbit coupling effect. Because of the frozen orbital angular momenta of the 3d-orbit for Fe atoms in Fe–Ga magnetostrictive alloys and the spin–orbit coupling, the distribution of the electron cloud is not isotropic, which leads to the anisotropy of exchange interaction between the different atoms. A method on estimating the magnetocrystalline anisotropy of Fe–Ga alloys by means of calculating orbit-projected density of states for Fe atoms is performed. The anisotropic distribution of the electron cloud of Fe atoms in these three crystalline structures of Fe–Ga is studied based on the above method showing the highest magnetic anisotropy for B2-like structure. This qualitative method comes closer to physical reality with a vivid physical view, which can evaluate the anisotropy of electron cloud for 3d transition atoms directly. The calculated results are in good agreement with both the previous theoretical computation and the tested value on the magnetic anisotropy constant, which confirms that the electron cloud anisotropy of Fe atoms could well characterize the magnetocrystalline anisotropy of Fe–Ga magnetostrictive material.

**Keywords:** Fe–Ga magnetostrictive alloy, magnetocrystalline anisotropy
**PACC:** 7580, 7530G

## 1. Introduction

In recent years, the magnetostrictive material containing transition metal, such as Fe–Ga alloy, has received much attention because of the attractive characteristics of large magnetostriction values at low saturation fields, high mechanical strength, good ductility and low associated cost.[1−6] But the experimental data of magnetostriction for Fe–Ga alloys fluctuate within a wide range,[7−11] and the spontaneous magnetostriction of Fe–Ga alloys is still unknown. So calculating the magnetocrystalline anisotropy by first-principles arouses extensive interest,[12−16] which causes the spontaneous magnetostriction directly.

Some investigations on calculating the magnetocrystalline anisotropy of 3d alloys by first principles have been reported in several different methods. Trygg *et al* [17] performed the total energy calculation of the magnetocrystalline anisotropy energy (MAE) based on the local spin density approximation (LSDA) of density functional theory including an orbital polarization correction and the spin–orbit coupling self-consistently within a scalar relativistic theory. They obtained the correct easy magnetization axis and the relatively good agreement of the value of the MAE with experiment for bcc Fe, fcc Co, and hcp Co, but failed to give the correct easy axis for fcc Ni. Razee *et al* [18] calculated the MAE directly within the fully relativistic effects instead of subtracting the total energies for two magnetization directions separately. This approach treats the spin–orbit coupling and spin-polarization on an equal footing in place of treating the spin–orbit coupling as a perturbation, and gets the reasonable MAE as well as the magnetic easy axis of bcc Fe, fcc Co, and fcc Ni. Wang and Wu *et al* proposed the state-tracking[19] and the torque methods[20] which only need to calculate MAE at one particular magnetic orientation, and are used to calculate the MAE of the multilayer as well as the bulk alloys. Since the spin–orbit coupling is very weak in 3d transition metals, and the total energy of the system is several orders of magnitude larger than its MAE ($\sim \mu$eV),[12,16] which is always treated as a perturbation to the total energy of the system, it is a

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tough work to get the calculated numerical value of the MAE for 3d transition alloys by first principles. Wu[12] calculated the MAE of Fe–Ga alloys based on the torque methods, while high precision and lots of workloads are required during the calculation. So a simple and easy way for rapidly evaluating magnetocrystalline anisotropy is demanded when designing a new magnetostrictive material.

In this paper, a new method on calculating the magnetocrystalline anisotropy is proposed to evaluate the magnetostriction for Fe–Ga alloys. This method expresses the anisotropic interaction between different atoms directly by studying anisotropic distributions of the electron cloud due to the spin–orbit coupling and crystal field effect. Though it is qualitative to some extent, the proposed method gives a vividly physical view and a direct calculation of the magnetocrystalline anisotropy for 3d transition magnetostrictive material.

## 2. Calculated models and methods

The self-consistent full-potential linearized augmented plane wave (FLAPW) method[21] based on the generalized gradient approximation (GGA) within the density functional theory is applied to calculate the electronic structure of Fe–Ga alloys with $D0_3$, B2-like and $L1_2$ crystalline structures. The wave functions are expanded in spherical harmonics within nonoverlapping spheres, while the plane waves are used in the outer space, thus, no shape approximations are made to the charge densities, potentials, and matrix elements. The core and valence states are both treated by a fully relativistic effect in a central-field approximation with the spin–orbit coupling, and the spin–orbit coupling effect is exerted along the [001] direction. The GGA formulas proposed by Perdew *et al* [22] are used for describing the exchange-correlation potential. Figure 1 shows the investigated models of $D0_3$, B2-like and $L1_2$ crystalline structures in Fe–Ga alloys, the inequivalent atoms of $Fe_I$ and $Fe_{II}$ are expressed with the different icons. (see Fig.1). A minimization of the total energy with volume is performed in order to determine the theoretical equilibrium volume for these structures. Hence, the lattice constants, $a = 6.91$ a.u., for cubic $L1_2$ structure, and $a = 7.694$ a.u., $c = 10.881$ a.u., for quasicubic $D0_3$ structure are used to calculate the electronic structure. B2-like is considered to be same as the modified $D0_3$, the equilibrium lattice constants of $D0_3$ structure are used for the unstable B2-like structure.[6] The muffin-tin sphere radii used are 2.0 a.u. for Fe atoms, whereas 2.1 a.u. for Ga atoms. The number of plane wave $R_{\mathrm{mt}}K_{\max}$ is up to 9, and lattice harmonics with angular momentum l up to 6 are adopted within the muffin-tin spheres to expand the charge density, potential, and wave functions. Fourier expansion for the charge density $g_{\max}$ was taken up to 14. The charge criterion is chosen to achieve convergence, which is taken at $10^{-6}$ Ry, and more than 585 $k$ points for $D0_3$ and B2-like structures, and 550 $k$ points for $L1_2$ structure are used in the irreducible wedge of the first Brillouin zone to ensure convergence in the Brillouin zone integration.

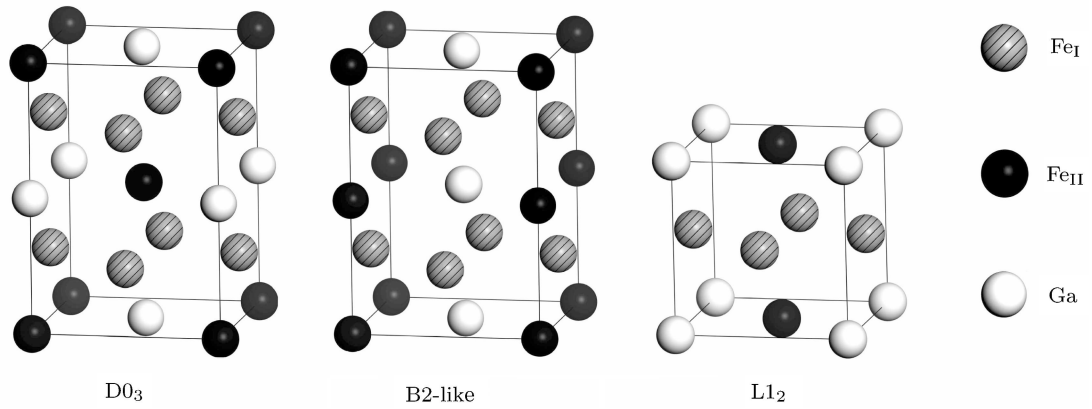



**Fig.1.** Representation of $D0_3$, B2-like and $L1_2$ structures for Fe–Ga alloys. Three sorts of inequivalent atoms are denoted by balls of different pattern, the streaked balls for $Fe_I$ atoms, whereas white and black balls for Ga and $Fe_{II}$ atoms, respectively.

## 3. Results and discussion

Fe–Ga magnetostrictive alloys with partially filled 3d shells of transition metal are strongly influenced by their crystalline environment, i.e. the crystal field effect, compared to the traditional magnetostrictive alloy TbDyFe with deeply lying $4f$ shells beneath $5s$ and $5p$ shells of rare earth elements.[23−26] Furthermore, for spin-polarized cases, depending on the direction of magnetization,[21] the spin–orbit coupling may lower the symmetry. So a cubic $L1_2$ system is also considered to have a tetragonal symmetry when the magnetization axis is along the easy axis [001] for Fe–Ga alloys. Table 1 lists the $3d$-orbit splitting and the electron occupancy of Fe atoms in $D0_3$, B2-like and $L1_2$ crystalline structures of Fe–Ga due to the crystal field effect and the spin–orbit coupling. The $d_{z2}$, $d_{xy}$ and $d_{(x2-y2)}$ orbits of $Fe_I$ and $Fe_{II}$ atoms in these three structures are all nondegenerate. And the $Fe_{II} - d_{xz}$ and $Fe_{II} - d_{yz}$ of all three structures are degenerate, but $Fe_I - d_{xz}$ and $Fe_I - d_{yz}$ of B2-like and $L1_2$ structures are nondegenerate. The less symmetry of the crystal field produces the lower degeneracy of the $3d$ orbit energy-level. For B2-like structure, the space point group of $Fe_I$ atoms is D2h, whereas D4h for $Fe_{II}$ atoms, so the $3d$-orbit of $Fe_I$ atoms in B2-like is completely nondegenerate, however $d_{xz}$ and $d_{yz}$ orbits for $Fe_{II}$ atoms are degenerate. Because of the lifting of degeneracy of $3d$ orbits, the orbital angular momenta of Fe atoms in Fe–Ga alloys are frozen due to the crystal field effect, and the orbital motions of the magnetic electrons are strongly tied to the lattice. Then through the spin–orbit coupling, the atomic spin is also tied to the crystal lattice, so the anisotropies of the orbital and spin moment are produced. When a magnetic field is applied, changing the direction of spin and orbital motion will need an extra energy, i.e. MAE, due to the crystal field effect and the spin–orbit coupling for Fe–Ga alloys. So it is the crystal field effect and the spin–orbit coupling effect which cause the magnetocrystalline anisotropy in Fe–Ga magnetostrictive material. It is clear that in B2-like the orbital angular momentum of $Fe_I$ atoms is completely quenched based on the results in Table 1, whereas the orbital angular momentum of $Fe_I$ in $D0_3$ structure is partially quenched. So the spin–orbit coupling performs a more vital role to rotate the orbital motion on B2-like structure due to the more strongly tied orbital motions and so the magnetocrystalline anisotropy will be larger. Our prediction of magnetocrystalline anisotropy based on the situation of orbital angular momentum quenching is well consistent with the result of Wu.[12]

The electron occupancies of Fe atoms in $D0_3$, B2-like and $L1_2$ crystalline structures of 3d orbits are listed in Table 1 based on the calculated orbit-projected density of states by FLAPW. The spin–orbit coupling effect is along the [001] direction. Then, the question is how to characterize the magnetocrystalline anisotropy of Fe–Ga alloys based on the results of the electron occupancy of Fe atoms in these three structures.

**Table 1.** Calculated electron occupancy ($e^-$/atom.spin) and the orbit splitting of Fe atoms in $D0_3$, B2-like and $L1_2$ crystalline structures for Fe–Ga alloys.

unit: $e^-$/atom. spin

| structures | atom sites | electron occupancy | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | majority spin | | | | | | minority spin | | | | | |
| | | $d$ | $d_{z2}$ | $d_{xy}$ | $d_{(x2-y2)}$ | $d_{xz}$ | $d_{yz}$ | $d$ | $d_{z2}$ | $d_{xy}$ | $d_{(x2-y2)}$ | $d_{xz}$ | $d_{yz}$ |
| $D0_3$ | $Fe_I$ | 3.83812 | 0.76260 | 0.77046 | 0.76311 | 1.54195 | | 1.90383 | 0.34379 | 0.40616 | 0.34294 | 0.81094 | |
| | $Fe_{II}$ | 4.05296 | 0.86275 | 0.86435 | 0.77516 | 1.55070 | | 1.63051 | 0.13434 | 0.13422 | 0.45408 | 0.90787 | |
| B2-like | $Fe_I$ | 3.84720 | 0.76985 | 0.77694 | 0.77037 | 0.74932 | 0.78072 | 1.88739 | 0.33894 | 0.35311 | 0.42301 | 0.48859 | 0.28374 |
| | $Fe_{II}$ | 4.05129 | 0.86001 | 0.86334 | 0.76231 | 1.56563 | | 1.60727 | 0.17845 | 0.14107 | 0.41581 | 0.87194 | |
| $L1_2$ | $Fe_I$ | 4.01447 | 0.81483 | 0.77712 | 0.83607 | 0.77715 | 0.80930 | 1.66326 | 0.31523 | 0.45359 | 0.21514 | 0.45352 | 0.22578 |
| | $Fe_{II}$ | 4.01444 | 0.84642 | 0.80942 | 0.80426 | 1.55434 | | 1.66325 | 0.16506 | 0.22581 | 0.36538 | 0.90700 | |

The force between spins of atoms is the exchange interactions, but it is well known to be isotropic and not to lead to any anisotropy because the scalar product $S_i \cdot S_j$ is independent of both the crystal structure and the choice of the coordinate system. Van Vlerk[27] considered the anisotropy resulting from the inter-

play between spin–orbit coupling and the so-called orbital valence. The orbital valence focuses on the anisotropic electrostatic interaction between the different atoms, and a mathematical expression in formulas is suggested by Van Vlerk.[27] The energy of orbital valence has the form $f(L_i \cdot L_j,\ L_i \cdot r_{\mathrm{Ij}},\ L_j \cdot r_{\mathrm{Ij}})$,[27] which does not appear in the Heisenberg exchange interaction, but it is formally equivalent to isotropic spin-spin coupling energy $F(S_i \cdot S_j)$. So the coupling between orbital angular momentum vectors of different atoms is a vital ingredient according to this mathematical expression. However, as mentioned above, the orbital angular momenta of the Fe atoms in Fe–Ga alloys are almost completely quenched due to the crystalline field effect based on the results in Table 1. How the orbit couplings between the neighbouring atoms perform? It is known that the orbit-lattice couplings in Fe–Ga alloys are very strong because of the forcefully tied orbit motion as mentioned before, so the spin-lattice couplings are in effect due to the spin–orbit coupling. Through the evident spin-spin exchange interactions, the orbit-orbit coupling is implemented. That is to say, the interplay between orbital angular momentum vectors of different atoms can be represented by the exchange interaction between the anisotropic electron distributions of different atoms in view of the non-negligible spin–orbit coupling.

The anisotropic distribution of the electron of Fe atoms along the easy magnetization axis [001] ($\Delta n^{[001]}_{\mathrm{anisotropic}}$) can be expressed by subtracting the ideally isotropic electron occupancy ($n_{\mathrm{Isotropic}}$) from the practical ones ($n_{\mathrm{practical}}$)

$$\Delta n^{[001]}_{\mathrm{anisotropic}} = n^{[001]}_{\mathrm{practical}} - n^{[001]}_{\mathrm{Isotropic}}. \tag{1}$$

The distribution of the electron occupancy along the easy magnetization axis [001] ($n^{[001]}$) is considered due to both the charge density of $d_{z^2}$ orbit and the contributions of the $d_{xz}$ and $d_{yz}$ orbits along the easy axis [001], as shown in the following equation:

$$n^{[001]} = \frac{\sqrt{2}}{2}\left(n\left(d_{xz}\right) + n\left(d_{yz}\right)\right) + n\left(d_{z^2}\right). \tag{2}$$

The ideal isotropic electron occupancy ($n_{\mathrm{Isotropic}}$) for one certain state in the $3d$ orbit of Fe atom, such as $n_{\mathrm{Isotropic}}(d_{z^2})$, is from the one fifth of the total electron occupancy of $3d$ orbit ($n_{\mathrm{d}}$). So equation (2) for the ideally isotropic electron occupancy can be expressed as

$$n^{[001]}_{\mathrm{Isotropic}} = \frac{\sqrt{2}}{2}\left(\frac{n(\mathrm{d})}{5} + \frac{n(\mathrm{d})}{5}\right) + \frac{n(\mathrm{d})}{5}. \tag{3}$$

By introducing Eqs.(2) and (3) into Eq.(1), we finally have:

$$\Delta n^{[001]}_{\mathrm{anisotropic}} = \left[\frac{\sqrt{2}}{2}\left(n_{\mathrm{practical}}\left(d_{xz}\right) + n_{\mathrm{practical}}\left(d_{yz}\right)\right) + n_{\mathrm{practical}}\left(d_{z^2}\right)\right] - \frac{\sqrt{2}+1}{5} n(\mathrm{d}). \tag{4}$$

Using Eq.(4) and the data from Table 1, we show the results of the $\Delta n^{[001]}_{\mathrm{anisotropic}}$ in these three crystalline structures of Fe–Ga in Fig.2(a), whereas figure 2(b) depicts the absolute value of the anisotropic distribution

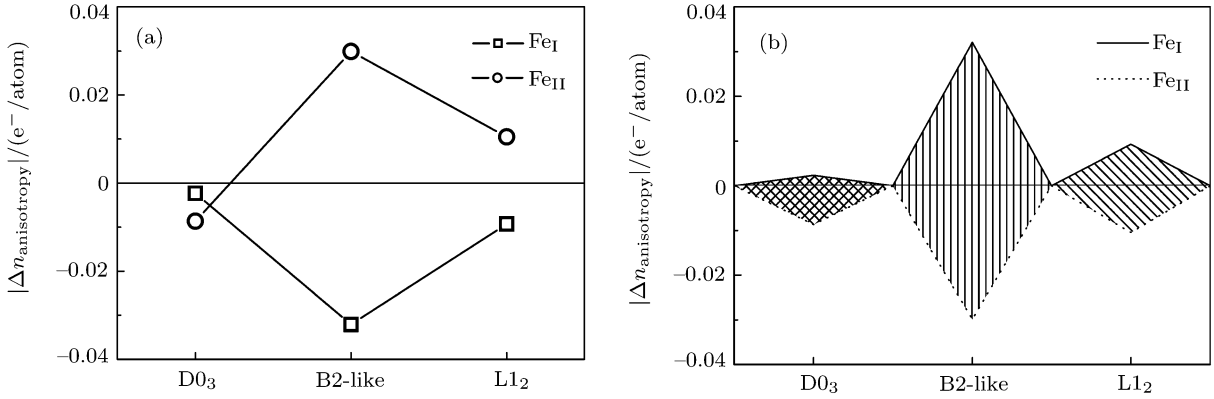



**Fig.2.** The calculated anisotropy of electron occupancy along the easy magnetization axis (001) for Fe atoms in $\mathrm{D0_3}$, B2-like and $\mathrm{L1_2}$ structures of Fe–Ga alloys. It shows the anisotropic distribution of the electron cloud along (001) direction [see Eq.1]. (b) The absolute value of data in Fig.2(a). The upper half is for $\mathrm{Fe_I}$ atoms, and lower half is for $\mathrm{Fe_{II}}$ atoms. It is shown by the filled area with three kinds of patterns to distinguish the different structures, so the magnitude for anisotropic distributions of the electron cloud is clear at a glance. This quomodo is adopted for a good vision effect, and the filled acreage has no specific physical significations.

of the electron cloud of Fe–Ga alloys. As shown in Fig.2(a), the anisotropic distribution of the electron cloud is –0.03209e$^-$ for $Fe_I$ atoms and 0.02989e$^-$ for $Fe_{II}$ atoms in B2-like, while –0.00232e$^-$ for $Fe_I$ atoms, and –0.00866e$^-$ for $Fe_{II}$ atoms in $D0_3$, and –0.00926e$^-$ for $Fe_I$ atoms and 0.01048e$^-$ for $Fe_{II}$ atoms in $L1_2$. It is clear in Fig.2(b) that the upper half and the lower half of the pattern are almost symmetrical, so the $Fe_I$ and $Fe_{II}$ atoms of the same structures undergo both the crystal field effect and the spin–orbit coupling effect almost at the same order.

It is easy to know that the larger anisotropy of the electron cloud distribution generates the larger anisotropy of electron exchange interaction between different atoms due to the spin–orbit coupling effect, and then the coupling between orbital angular momentum vectors of different atoms is larger. As a result, the higher magnetocrystalline anisotropy is obtained based on the theory of Van Vlerk.[27] So the highest magnetic anisotropy constant will be gotten in B2-like structure, which contains the largest anisotropy of the electron cloud distribution in Fig.2(b), and $D0_3$ reveals the lowest one. Based on the result of the anisotropy of the electron cloud in Fig.2(b), the ascending sequence of the absolute value of magnetic anisotropy constant is considered to be

$$|K_{\mathrm{B2-like}}| > |K_{\mathrm{L1_2}}| > |K_{\mathrm{D0_3}}| .$$

The empirical relation of $\lambda_{001} = \dfrac{2K}{3\,(C_{11} - C_{12})}$ from magnetoelastic theory[28–30] indicates the connection between magnetostriction and magnetic anisotropy for a bulk system, and the magnetostriction is monotonic with respect to the magnetic anisotropy in Fe–Ga alloys.[12] Because of the highest absolute value of the magnetic anisotropy constant for B2-like structure and the direct relation between magnetostrictive coefficient and magnetic anisotropy constant, it can be forecasted that B2-like structure can produce the highest magnetostrictive coefficient in Fe–Ga alloys. Based on the calculated magnetic anisotropy results, the sequence of magnetostrictive coefficients in Fe–Ga alloys is

$$|\lambda_{\mathrm{B2-like}}| > |\lambda_{\mathrm{L1_2}}| > |\lambda_{\mathrm{D0_3}}| .$$

Obviously, the B2-like structure possesses the much larger magnetic anisotropy than both $D0_3$ and $L1_2$ structures, as shown in Fig.2(b). Lograsso *et al*[5] mentioned that B2-like structure may play a key role in the giant magnetostriction in Fe–Ga alloys based on the indirect experimental evidence, and this is well consistent with our results. The calculated values of magnetostrictive coefficient in Ref.[11] are +380 ppm, –298 ppm, and –107 ppm for the B2-like, $L1_2$ and $D0_3$ structures, respectively, it also proves the validity of the sequence of magnetostrictive coefficients for Fe–Ga alloys obtained above. So the method on evaluating the magnetostriction of Fe–Ga alloys by studying the anisotropic distributions of the electron cloud due to the spin–orbit coupling and crystal field effect is proved to be reliable. In general, the results of the magnetic anisotropy are in good agreement with both the previous theoretical computation and the experimental measurements. It demonstrates that the electron cloud anisotropy of Fe atoms can well characterize the magnetocrystalline anisotropy of Fe–Ga magnetostriction material. And more, our method is much easier to perform because of avoiding the arduous work of calculating the subtle value of magnetocrystalline anisotropy energy, so it is a quick way for designing a new magnetostrictive material.

## 4. Conclusions

A simple method on evaluating magnetocrystalline anisotropy is proposed by calculating the anisotropic distribution of the electron cloud for Fe atoms in Fe–Ga magnetostrictive alloys. A large magnetostriction is expected in B2-like structure rather than $D0_3$, and $L1_2$ structures of Fe–Ga alloys judged by this method.

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