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Total Energy Calculation of the Magnetocrystalline Anisotropy Energy in the Ferromagnetic 3*d* Metals

J. Trygg,[1] B. Johansson,[1] O. Eriksson,[1] and J. M. Wills[2]
[1]*Condensed Matter Theory Group, Department of Physics, University of Uppsala, P.O. Box 530, S-75121, Uppsala, Sweden*
[2]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
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We demonstrate that total energy calculations based upon only the local density approximation of density functional theory in combination with an orbital polarization correction can be used to derive the magnetocrystalline anisotropy energy (MAE) for the ferromagnetic metals, bcc Fe, hcp Co, fcc Co, and fcc Ni. In the case of bcc Fe, hcp Co, and fcc Co the calculations reproduce the experimental easy axis as well as the size of the MAE. However, for fcc Ni we obtain the wrong easy axis.

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The calculation of the magnetocrystalline anisotropy energy (MAE), i.e., the difference in energy when the magnetization is pointing in two different directions, has for a long time been an outstanding problem for the 3*d* ferromagnetic elements [1]. It was suggested earlier that the coupling between the magnetization and the lattice, arising through the spin-orbit interaction, in combination with an energy band picture, will provide a MAE of the right order of magnitude for bcc Fe, hcp Co, and fcc Ni [2]. Several investigations have been reported within this approach, and one of the conclusions drawn from these studies is that the technical problems in resolving the extremely small energy differences which are needed are very hard to overcome. Previously, an investigation of the magnetocrystalline anisotropy energy for the late 3*d* transition metals, using a standard energy band calculation method in conjunction with the local spin density approximation (LSDA), was reported [3]. While the magnitude of the MAE (of the order of μeV) was correctly obtained for all three metals, the wrong easy axis was obtained for hcp Co and fcc Ni, and, moreover, the number of k points was unduly large. The calculations presented by Daalderop, Kelly, and Schuurmans [3] were based on a geometrical constraint on the charge and spin density of the crystal as well as of the shape of the crystal potential through the use of the atomic sphere approximation (ASA). Further, the so-called force theorem [4] was used to evaluate the energy difference between two spin directions. However, due to the development of more efficient and faster computers in combination with recent advances in accurate total energy methods, we will in this Letter demonstrate that it has now become possible to calculate the MAE for the 3*d* elements directly from the total energy in a self-consistent way. This is a most desirable development since from previous theoretical work one could not draw conclusions about whether the disagreement between experiment and theory was due to limitations of the calculational method or due to the errors associated with the LSDA. Previously, the total energy difference approach was used to calculate the MAE for uranium sulphide (US) [5]. However, its MAE is 10^4 times larger than for the 3*d* elements and does not call for the special treatment we address in this present Letter.

Here we present results that go beyond the above mentioned approximations. As a matter of fact, the only major approximation made here is the LSDA of density functional theory, used to handle the electron many-body problem. Accordingly, we will calculate the total energy by means of a method which does not rely on geometrical constraints on the charge density, the spin density, and the potential. The calculations presented here are based on a full potential method [6] modified to be able to treat the MAE problem. Since a total energy calculation of this kind, with a tremendous requirement on the energy resolution for the 3*d* ferromagnets, is a most delicate task (and for this reason has not been done until now), we will describe the calculations in some detail below and the special care one has to exercise when performing theoretical calculations of the MAE. Also, we will point out the different convergence tests we have performed to ensure that the calculations have reached the required accuracy.

The potential is divided into a base geometry consisting of a muffin-tin region and an interstitial region. The spin-orbit interaction was added to the Hamiltonian matrix in the way suggested by Andersen [7]. The basis functions are linear combinations of augmented, linear muffin-tin orbitals through $\ell = 2$ [7,8]. The radial parts of the basis function inside the muffin tin were calculated using the scalar relativistic representation [9]. In the parent muffin-tin sphere, basis functions were expanded in spherical waves through $\ell = 8$, whereas the electronic density, spin density, and potential were expanded in a spherical harmonic series through $\ell = 8$ and where the full symmetry of the lattice has been taken into account to reduce the number of harmonics used in the expansion. In the interstitial region for bcc Fe, fcc Co, and fcc Ni, the Fourier series was truncated at (see discussion below) $g_{\max} \sim 8$ (in units of $2\pi/a$) for the basis functions and

$g_{\max} \sim 14$ for the electron density and potential. For hcp Co the Fourier series was truncated at $g_{\max} \sim 5.9$ for the basis functions and $g_{\max} \sim 10.5$ for the electron density and potential. We performed several test calculations with a larger number of plane waves in the Fourier expansion, but no change was found in the MAE. Furthermore, in order to ensure that the expansion of the wave functions is well converged we used a double basis set. Thus the total matrix size is 36×36 for bcc Fe, fcc Co, and fcc Ni, and 72×72 for hcp Co. As a test we also carried out a calculation for fcc Ni, where we used more basis functions (triple basis, with a matrix size of 54×54). However, this extension resulted in a totally negligible change in the MAE. Thus the use of a double basis set is sufficient to ensure that the wave function is well converged. For the **k**-space integration we used the so-called special point method [10,11] with a Gaussian broadening of 10–15 mRy for states close to the Fermi energy. We also performed a test calculation for fcc Ni with a Gaussian width of 5 mRy, to see to what extent the broadening influences the MAE. However, we found no significant change in the calculated MAE upon modification of this width.

Depending on the direction of the quantization axis of the spin, the number of symmetry operations of the system will be different [12]. Because of that, some caution regarding the computational details has to be made. First of all, the irreducible part of the Brillouin zone (BZ) is different in the two cases. Secondly, since we are using a Fourier series expansion of the density as well as the potential and wave function in the interstitial region, the errors made when truncating these series will be different for the two spin quantization cases [13]. In order to check the accuracy of the method, and to make sure that no systematic errors were introduced, we first performed energy band-structure calculations for two different magnetization directions with the spin-orbit interaction set equal to zero. This was done for a large number of k points to ensure that the sampling of the BZ was well converged, and with the spin quantized along [001] and [111] for bcc Fe, fcc Co, and fcc Ni, and [0001] and $[10\bar{1}0]$ for hcp Co. The total energy difference between the two different spin orientations was found to be less than 0.05 μeV for all four test cases. Thus this convergence test shows that our method has the capability to give total energy differences of extremely high accuracy.

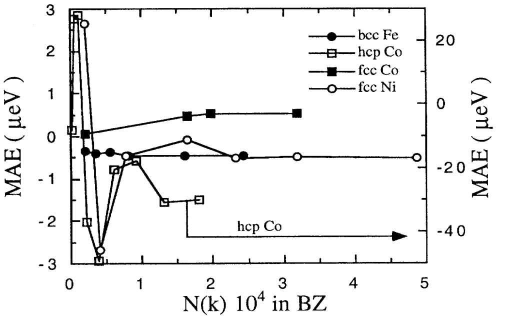

FIG. 1. Convergence of the magnetocrystalline anisotropy energy for bcc Fe, fcc Co, fcc Ni, and hcp Co as a function of the number of k points, $10^4 N(k)$, in the full Brillouin zone. The scale to the right refers to hcp Co.

Next we included the spin-orbit interaction and then performed self-consistent calculations [14] (denoted SO here) for the mentioned two different spin directions in bcc Fe, hcp Co, fcc Co, and fcc Ni. One of the problems one faces in this kind of calculation is that the sampling of the BZ has to be performed with extreme care and the total energy needs to be converged with respect to the number of k points used for sampling the irreducible part of the BZ. To illustrate this we show in Fig. 1 the calculated MAE as a function of the number of k points. We notice that to achieve convergence in the number of k points, we need about 15 000 k points in the full BZ for bcc Fe, fcc Co, and hcp Co and slightly more for fcc Ni, around 25 000 k points. However, the number of k points used in the irreducible wedge for the lowest symmetry direction is around 2000 k points for bcc Fe and 6000 for hcp Co, fcc Co, and fcc Ni. Although those are large numbers they are considerably smaller than what had to be used in the calculation in Ref. [3], where ~500 000 k points in the irreducible part of the BZ were needed for fcc Ni. Regarding the calculated values of the MAE, we see from Table I that for bcc Fe and fcc Co we calculate the correct easy axis [001] and [111], respectively, but that the magnitude of our theoretical values is lower than experiment. For hcp Co we also reproduced the experimental easy axis [0001], but again the magnitude of the calculated MAE is smaller than experiment. For fcc Ni the agreement between theory and experiment is less satisfactory, and we actually failed to obtain the correct easy axis [111]. It thus seems that our theoretical (LSDA) calculations account for the MAE of bcc Fe, fcc Co, and hcp Co fairly well, but fail in reproducing fcc Ni. Previously [3], the MAE of fcc Ni was calculated for different values of the number of valence electrons (which is 10 for

TABLE I. Experimental [20] and calculated magnetocrystalline anisotropy energy for bcc Fe, fcc Co, hcp Co, and fcc Ni. SO refers to the calculations using spin-orbit only, while OP refers to calculations where both spin-orbit and orbital polarization have been included. The units are in μeV/atom.

	Theory		
Atom	SO	OP	Experiment
bcc Fe	−0.5	−1.8	−1.4
hcp Co	−29	−110	−65
fcc Co	0.5	2.2	1.8[a]
fcc Ni	−0.5	−0.5	2.7

[a] Reference [21].

Ni). This is a sensible test since it is possible that calculations based on the local density approximation may, for instance, overestimate the *d* occupation of the 3*d* states. Therefore it is interesting to investigate to what extent the MAE of Ni depends on small changes in the number of valence electrons or equivalently how sensitive it is regarding the exact position of the Fermi energy. We have performed similar test calculations for fcc Ni by letting the nuclear charge vary around 28, while maintaining charge neutrality in the system. This is usually referred to as the virtual crystal approximation (VCA) [15]. We have calculated the MAE as a function of the number of valence electrons and find that the resulting MAE is a smooth function in the interval of 9.8 to 10.1, with no change of sign. This shows that the problem of obtaining the correct easy axis for fcc Ni is not likely to originate from possible errors in the calculated population of the *d* orbitals.

The disagreement between the calculation of the MAE in Ref. [3] and experiment was discussed by Jansen [16]. He concluded that the energy density functional together with the spin-orbit coupling must contain terms which depend directly on the orbital moment. In order to investigate this possibility we added to the Hamiltonian an orbital-correction term in the same way as has been described previously [17]. This is an approximate way to account for Hund's second rule, well known in atomic theory [18]. In these calculations (denoted OP here) we have chosen the same *k* point sets as those we used above, where we know that the MAE is converged (see Fig. 1). In Table I we list the resulting values for the MAE and we note that an enhancement factor of 3 to 4 is obtained for bcc Fe, fcc Co, and hcp Co when the orbital polarization is included. The value of the MAE is in good agreement with experiment for bcc Fe and fcc Co, and in acceptable agreement for hcp Co. On the other hand, for fcc Ni we obtained no enhancement of the MAE when the orbital correlation is taken into account. Thus even after the inclusion of the orbital polarization our theory still fails to give the [111] direction as the easy axis for fcc Ni. In Fig. 2 we display the calculated value of the MAE for the SO and OP calculations together with experiment. Note that the MAE of hcp Co is an order of magnitude larger than for the cubic systems. From the upper panel in Fig. 2 we see that, except for fcc Ni, the agreement with experiment is in fact very good for the OP calculation, since we must remember that these energies are extremely small quantities and very difficult to calculate.

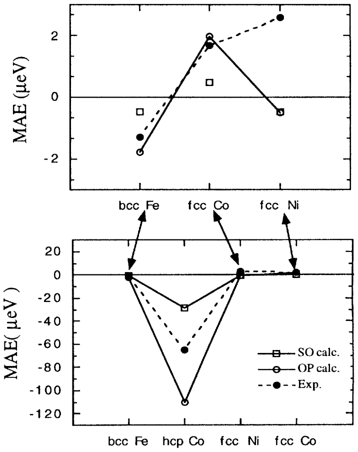

FIG. 2. The magnetocrystalline anisotropy energy in bcc Fe, hcp Co, fcc Co, and fcc Ni for spin-orbit calculation (SO), and the orbital polarization calculation (OP), compared to experiment [20]. The upper panel shows the MAE for bcc Fe, fcc Co, and fcc Ni. The lower panel includes the result for hcp Co.

In Table II we list the calculated and experimental spin and orbital moments. The theoretical values are given for the two quantization axes. Note first of all that the spin moments are insensitive to whether or not we include the orbital polarization. In contrast, for the orbital moment the situation is different and the OP calculations give orbital moments which are enhanced by 40%–60%. For the OP calculations the agreement between theory and experiment is quite good, for both the spin and orbital moments. Other theoretical data for bcc Fe, hcp Co, and fcc Ni, which neglect orbital polarization effects, typically give orbital moments which agree with the SO data in Table II. Thus this shows the importance of orbital polarization effects. This conclusion was previously reached by Söderlind, Eriksson, and Johansson [19], who studied bcc Fe, hcp Co, and fcc Ni by means of the linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA). The presently calculated spin and orbital moments agree quite well with those presented previously [19], and from this point of view the ASA seems to be a good approximation. However, a new and interesting feature of the present calculations is that there is a slight anisotropy in the size of the orbital moment, depending on which spin quantization axis is used. This effect is most pronounced for hcp Co, where the change is of the order of 4%. Unfortunately we are not aware of any experimental data concerning this issue.

When comparing the results of Tables I and II we observe the following. The inclusion of the OP is important for both the MAE and the orbital moment itself. Inclusion of orbital polarization effects improves the agreement with experiment for both properties. For the analysis of the different terms in the total energy expression, we conclude that generally the MAE is dominated by the orbital polarization term. In addition, we observe that for both levels of approximation (SO and OP) the calculated easy axis always has the largest orbital moment. This effect is already present at the SO level, where the orbital correction term is absent. This observation leads us to speculate that a possible way to identify the easy magnetization axis

TABLE II. Experimental [20] and calculated spin, μ_s, and orbital moments, μ_ℓ, for bcc Fe, fcc Co, hcp Co, and fcc Ni. The superscript SO refers to calculations using spin-orbit only, while OP refers to calculations where both spin-orbit and orbital polarization have been included. The calculations have been performed for two different magnetization axes. All moments are in units of μ_B.

		μ_s^{SO}	μ_ℓ^{SO}	μ_s^{OP}	μ_ℓ^{OP}	μ_s^{exp}	μ_ℓ^{exp}
bcc Fe	[001]	2.1928	0.0485	2.1934	0.0783	2.13	0.08
	[111]	2.1928	0.0484	2.1934	0.0781	⋯	⋯
hcp Co	[0001]	1.5898	0.0765	1.5905	0.1232	1.52	0.14
	$[10\bar{1}0]$	1.5898	0.0762	1.5905	0.1185	⋯	⋯
fcc Co	[001]	1.6184	0.0745	1.6187	0.1180	⋯	⋯
	[111]	1.6184	0.0746	1.6187	0.1182	⋯	⋯
fcc Ni	[001]	0.6085	0.0475	0.6109	0.0655	⋯	⋯
	[111]	0.6085	0.0475	0.6109	0.0654	0.57	0.05

might simply be to calculate the orbital moments for the different directions, and the easy axis is the direction where the orbital moment is largest.

To conclude, we have demonstrated that it is possible to perform highly accurate total energy calculations for the MAE of bcc Fe, fcc Co, hcp Co, and fcc Ni. We have also shown that orbital polarization effects are important both for the size of the orbital moment as well as for the MAE itself. For bcc Fe, fcc Co, and hcp Co our calculations give the correct easy magnetization axis and a value of the MAE which is in relatively good agreement with experiment. For fcc Ni our calculations give the wrong easy axis. Since the number of approximations in the calculations have been reduced to a minimum, we have to conclude that this remaining failure reflects a limitation of the LSDA in the case of fcc Ni.

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