Static non-uniform magnetic susceptibility of selected transition metals

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Abstract. A theoretical basis is given for the determination of the static, but wave-vector dependent, magnetic susceptibility (unenhanced and enhanced). It is based on the local density approximation and is applied to the transition metals V, Cr, Rh, Pd as well as Fe, Co and Ni. In the first group we contrast the susceptibility behaviour of Cr with that of Pd both of which are near a magnetic instability, and compare these behaviours with that of V and Rh. In all cases the Stoner parameter $I(q)$ is obtained and discussed. Our results for the magnetic metals in the second group clearly distinguish the two forms of Fe, FCC-Fe having a non-collinear and BCC-Fe a ferromagnetic ground state. For FCC-Co, HCP-Co, and Ni the self-consistently determined magnetic moments were found to vanish for q larger than 0.6, 0.9 and 0.5 in $(0, 0, q)$ $(2\pi/a)$, respectively. Near these values of the wave vector the enhanced susceptibility peaks strongly. Our results for the magnetic susceptibilities are compared with results of other calculations.

1. Introduction

The determination of the wave-vector and frequency dependent magnetic susceptibilities of metals by first-principles calculations is of considerable importance and has, consequently, led to a great number of investigations [1–5]. The calculated quantities can be directly related to experimental data [6, 7], but, more importantly, they play a central role in theoretical descriptions of interacting electron systems [5, 8, 9]. Although some limited amount of physical information is contained in the unenhanced susceptibility [10, 11], it is the enhanced susceptibility that describes the physical system completely [6, 9].

Several techniques for calculating the wave-vector and frequency dependent, enhanced magnetic susceptibility exist [1, 2, 4]. They have many features in common and we may briefly comment on some of them. First, the electronic band structure for a crystal with no external magnetic field applied is needed to describe the state of the system. Second, the enhanced susceptibility is obtained as the solution of an integral equation that is derived by perturbation theory. The integral equation itself is solved using approximations. Third, the calculational schemes need, in addition to computer codes for determining the band structure, rather advanced programs for the evaluation of the susceptibility. Fourth, the mathematics is quite involved so for realistic calculations [1, 2] severe approximations are necessary; thus, for instance, only d bands were taken into account in the calculation of the magnetic response

by Cooke *et al* [1], and Callaway *et al* [2] neglected the wave function overlap at different sites.

The situation is considerably simpler for the case of the zero-frequency uniform susceptibility because in this case the response of the electronic band structure to a small applied magnetic field can be easily calculated [12–14] thus allowing both a determination of the enhanced static susceptibility [13, 14] and tests of approximate calculational schemes [13]. It is also possible to obtain limited information on the wave-vector dependence of the static, enhanced susceptibility by simulating a staggered magnetic field using supercell calculations [14]. As the supercell contains periodically repeated fragments of both the lattice and the magnetic field, their periods should be connected by a simple relation which will not result in an unreasonably large supercell. Thus any practical calculations cannot be carried out for magnetic fields incommensurate with the lattice, or for fields having a period many times larger than the period of the lattice. Therefore, the supercell approach is not suitable for obtaining the susceptibility as a continuous function of the wave vector.

A rather recent development in self-consistent field calculations makes possible an easy determination of both the enhanced and unenhanced zero-frequency magnetic susceptibility for any wave vector (including those incommensurate with the lattice). This is based on the generalized translational symmetry of the one-electron Hamiltonian of a spiral magnet as discussed some time ago by Herring [8]; this is also connected with the work of Korenman and Prange [15] as well as with that of Haines *et al* [17]. Herring's theory was applied to modern computational methods by one of us [18] and enables the calculations to be done self-consistently without resorting to any supercell geometry. A number of applications to real problems using spiral magnetic configurations [19, 20], have shown the efficiency and accuracy of this approach.

The objects of our calulations are the zero-frequency but wave-vector dependent unenhanced, χ_0, and enhanced, χ, magnetic susceptibilities of several transition metals. The standard relation [6] connecting these quantities for paramagnetic metals is

$$\chi = \frac{\chi_0}{1 - I \chi_0} \tag{1}$$

where the parameter I is often referred to as the exchange or Stoner parameter. In many cases this parameter is treated as a constant independent of the wave vector q, but a number of authors [3, 21, 22], did consider its wave-vector dependence. Thus, Vosko *et al* [22] suggested a theoretical approach to its q-dependence but did not apply it to a particular calculation, and in [3, 21] the wave-vector dependence of the exchange parameter was chosen arbitrarily to obtain a better description of neutron scattering experiments. Our calculations allow an estimate of the q-dependence of I on the basis of a first-principles approach. We will return to (1) in the next section where we give a simple derivation for both non-magnetic and magnetic systems.

The paper is organized as follows. In section 2 the theoretical background and some calculational details are described. Section 3 is devoted to calculations of the susceptibilities for the elemental metals V, Cr, Rh and Pd as well as Fe, Co and Ni, and in section 4 we summarize our results.

2. Calculational technique

To make this paper reasonably self-contained we give a brief description of the main

ideas underlying the theoretical method, stressing those points that distinguish it from conventional band-structure theory. At the basis is the local approximation to exchange and correlation [23] and the augmented spherical wave method (ASW), which are employed to carry out the self-consistent band-structure calculations [24]. This method was generalized by Uhl *et al* [20] to enable the treatment of spiral spin configurations.

The effective single-particle Hamiltonian for spin-polarized electrons forming a non-collinear magnetic structure may be written as [18, 20]

$$H = -\Delta + \sum_n U_n^+ V(|r - R_n|) U_n \tag{2}$$

where

$$V(r) = \begin{pmatrix} V_+(r) & 0 \\ 0 & V_-(r) \end{pmatrix} \tag{3}$$

is a potential in the local atomic frame of reference which is defined by setting the z axis parallel to the direction of the atomic moments. We shall call this the local coordinate system which may, in general, be different for each atom and which must be distinguished from the single, global coordinate system. The potentials V_σ ($\sigma = +, -$) are unambiguously given in the local coordinate system by means of functional derivatives [20, 25, 26], and the standard spin-$\frac{1}{2}$ rotation matrices U determine the transformation between the global coordinate system and the atomic systems [20].

A spiral magnetic structure is defined by

$$m_n = m \left(\cos(q \cdot R_n) \sin \vartheta, \sin(q \cdot R_n) \sin \vartheta, \cos \vartheta \right) \tag{4}$$

where m_n is the magnetic moment of the nth atom and $(q \cdot R_n)$ and ϑ are polar coordinates. It may be shown easily [8, 18] that the Hamiltonian (2) commutes with the operator $\{\alpha_n(q)|R_n\}$ of a generalized translation defined by

$$\{\alpha_n(q)|R_n\}\psi(r) = \begin{pmatrix} \exp\left(-\frac{1}{2}iq \cdot R_n\right) & 0 \\ 0 & \exp\left(\frac{1}{2}iq \cdot R_n\right) \end{pmatrix} \psi(r - R_n). \tag{5}$$

The quantity $\psi(r)$ is a bispinor function, and the operator $\{\alpha_n(q)|R_n\}$ combines a space translation by the vector R_n with a spin rotation of $(q \cdot R_n)$ about the global axis. These generalized translations form an Abelian group isomorphic with the group of ordinary space translations by the vector R_n. Therefore, the irreducible representations of both groups coincide and for the eigenfunctions of the Hamiltonian (2), there exists a generalized Bloch theorem

$$\{\alpha_n(q)|R_n\}\psi_k(r) = \exp(-ik \cdot R_n)\psi_k(r) \tag{6}$$

where the vectors k lie in the first Brillouin zone which is defined in the usual way by the vectors R_n. This means that for the actual calculations one only needs the chemical unit cell, and not a supercell.

A general starting point for a band-structure calculation is expansion of the Bloch bi-spinor function in the form

$$\psi_k(r) = \sum_{L\sigma} C_{L\sigma} \Phi_{L\sigma k}(r) \tag{7}$$

where, because of (6), $\Phi_{L\sigma k}$ may be written as a lattice sum

$$\Phi_{L\sigma k}(r) = \sum_n \exp(\mathrm{i}k \cdot R_n) U_n^+ \phi_{L\sigma}(r - R_n) \tag{8}$$

L denotes both angular momentum quantum numbers l and m, and $\sigma = 1, 2$ giving two possible bispinors $\phi_{L\sigma}$. Within the ASW method the latter are constructed using augmented spherical waves essentially as described previously [20, 26]. Of course, other methods like LMTO [19, 27] may be used instead. A standard Rayleigh–Ritz variational procedure now leads to the secular equation for spiral magnetic structures [20]. We emphasize some important points characterizing this method.

First, if the wave functions ψ_k satisfy the generalized Bloch theorem then the density matrix $\sum_k \psi_k \psi_k^+$ (the sum over occupied states is assumed) will be invariant under the action of a generalized translation. Therefore this symmetry is preserved in the numerical iteration process. Next, in non-collinear magnets the electron states given by (7) cannot be characterized by a definite spin projection. This leads to a doubling of the dimension of the secular equation as compared with the case of a ferromagnet since both up- and down-spin functions occur in the expansion, (7). Thus, in contrast to the traditional ferromagnetic case, the calculations cannot be carried out separately for up- and down-spin electrons. In fact, states of the non-magnetic or ferromagnetic system are shifted in reciprocal space by the wave vector q and interact, leading to hybridization [17, 18, 20, 28].

We now specify the form of the staggered magnetic field that is required in order to model the response of the itinerant electron system from which can be obtained the unenhanced and enhanced magnetic susceptibilities:

$$h(r) = \sum_n h \cdot (\cos(q \cdot R_n), \sin(q \cdot R_n), 0) \cdot \theta(|r - R_n|) \tag{9}$$

where $\theta(r)$ is the step function that equals unity for r smaller than the atomic sphere radius and zero otherwise. We emphasize that we only calculate the spin part of the susceptibilities and do not calculate orbital contributions. In order to simplify the calculations further we only deal with cases for which the magnetic moment of a given atom is parallel to the field. Therefore, in all calculations the magnetic structure is of the form given by (9), i.e. the magnetic moment of the nth atom should be parallel to the vector $(\cos(q \cdot R_n), \sin(q \cdot R_n), 0)$. For non-magnetic crystals this condition is always fulfilled because the symmetry of the unperturbed state (with no magnetic moments) guarantees that the field given by (9) and the induced moment are parallel.

For magnetic crystals one must ensure that this condition is fulfilled. To do this, the calculation is performed in two steps for every value of q. In the first step the calculations are carried to self-consistency constraining the symmetry of the magnetic structure so that it coincides with the symmetry of the magnetic field chosen. This field is then turned on and the response of the electrons is calculated. The symmetry of the crystal then guarantees that the magnetic response has the configuration of the field, as desired.

The detailed prescription for incorporating the magnetic field in both cases is simply the replacement of the unperturbed, self-consistent potentials V_σ in (3) by $V_\sigma - \sigma h$ ($\sigma = +, -$). The response after the first iteration now yields the unenhanced susceptibility, $\chi_0(q)$ whereas a full self-consistent calculation in the presence of this

field allows the system to relax the spin and charge densities, and hence yields the enhanced susceptibility, $\chi(q)$.

The desired wave-vector dependence of the exchange parameter $I(q)$ is obtained from (1) for which we now give a simple derivation that is valid for both non-magnetic and magnetic systems; it is based on the work of Callaway and Wang [29] as well as on that of Small and Heine [30].

The unenhanced susceptibility, by definition and calculation, describes the non-self-consistent response, Δm, to an applied magnetic field in the local coordinate system. The induced magnetic moment changes the exchange–correlation potential leading to an effective increase of the applied field. We may suppose that the effective field consists of the applied field, h, plus the exchange–correlation contribution, $I \Delta m$, again in the local system. Hence, the self-consistency condition is

$$\Delta m = \chi_0(h + I \Delta m) \tag{10}$$

and, therefore,

$$\Delta m = \chi h = \frac{\chi_0}{1 - I \chi_0} h \tag{11}$$

from which, trivially, (1) is obtained and

$$I(q) = \frac{1}{\chi_0(q)} - \frac{1}{\chi(q)}. \tag{12}$$

Finally we make use of the susceptibility to obtain an approximate expression of the total energy as a function of the amplitude of the magnetic moment for any value of the wave-vector q in the form [9]

$$E_q(m) = E_q(m_0(q)) + \frac{1}{2\chi(q)}(m - m_0(q))^2. \tag{13}$$

Here $m_0(q)$ is the self-consistent magnetic moment in the absence of a magnetic field and $E_q(m_0(q))$ is the total energy corresponding to this state. In passing we point out that the total energy function $E_q(m)$ can also be obtained using the 'fixed-moment scheme' [31] for $q = 0$ and with constrained calculations of the type discussed by [20, 32] for arbitrary q. However, in contrast to an evaluation of (13), these calculations are rather time consuming and will not be reported here.

In closing this section we point out that in the following calculations we used (as in [13]) a small magnetic field corresponding to a spin splitting of 2 mRyd. We convinced ourselves that for fields of this order the magnetic response is linear. A typical susceptibility deviation from a constant value does not exceed 1.5% for fields varying from 0 to 6 mRyd (in units of the spin splitting).

3. Susceptibility and the Stoner parameter

We chose to calculate the unenhanced and enhanced magnetic susceptibilities and Stoner parameters as functions of q for four non-magnetic and three magnetic metals, V, Cr, Rh, Pd, Fe, Co and Ni. Experimentally the ground state of Cr is magnetic. However, we have chosen the lattice constant such that the total energy is a minimum; this results in a slightly smaller lattice constant than observed and a non-magnetic ground state. Our results for $q = 0$ together with the lattice constants used and

Table 1. Parameters of calculation and calculational results for $q = 0$.

Metal	Crystal structure	Lattice parameters (au)	$\chi(0)$ (emu/mole × 10^{-4}) Present calculation	Others' results	$\chi(0)/\chi_0(0)$ Present calculation	Others' results	$I(0)$ (mRyd) Present calculation	Others' results
V	BCC	5.54	1.15		2.26	2.34[d]	26	26[d] 29[g]
		5.7	1.53	~ 1.6[a]	2.60	2.73[a]	25	
Cr	BCC	5.3	0.3		1.36	1.36[d]	28	28[d]
Rh	FCC	7.24	1.13	0.61[b]	2.04	1.79[d]	22	24[d] 20[b]
Pd	FCC	7.42	5.18	~ 7.1[a] 11.2[b]	6.85	4.46[d] 5.0[e] 4.6–9.4[a]	27	25[d] 24.5[b] 26[g]
Fe	BCC	5.27	0.21	0.37[c] 0.2[b]	1.24		28	34[d] 32.5[b] 33.5[f] 34[g] 30[c]
Fe	FCC	6.88	0.18		1.13		17	
Co	FCC	6.448	0.25	0.22[c]	1.00		0	36[d] 30[c] 36[g]
Co	HCP	4.738 7.690	0.14		1.23		32	
Ni	FCC	6.55	0.31	0.13[b] 0.26[c]	1.43		33	37[d] 34.5[b] 33[c] 37[g]

[a] [4]
[b] [44]
[c] [7]
[d] [13]
[e] [14]
[f] [45]
[g] [42]

results of other calculations (for comparison) are collected in table 1. In the case of V we also give the dependence of calculated values on the lattice constant, and in the cases of Fe and Co on the crystal structures.

In view of the different numerical techniques and, in some cases, the different lattice constants, the results are in reasonable agreement with each other. In the case of the non-magnetic metals the agreement achieved for the Stoner parameters is quite remarkable. However, in the case of BCC-Fe our value of I is somewhat less than the results obtained by other authors, and in the case of FCC-Co our findings are completely different. The reasons for this difference are discussed below.

We do not compare the calculated susceptibilities with experimental data because the orbital contribution which is of the order of 1–2 ×10^{-4} emu/mole [33] was not taken into consideration in our work. However, we note that in the case of Pd, where the spin contribution dominates, our value of the enhanced susceptibility is in good agreement with the experimental value of 7.1 emu/mole [34]. Our calculated susceptibilities, both unenhanced and enhanced, and the Stoner factors as functions
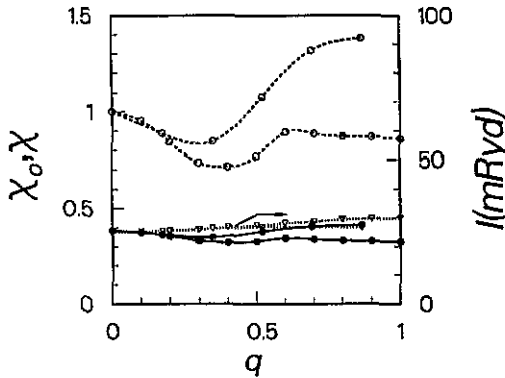
Figure 1. The q dependence of unenhanced and enhanced susceptibilities and of the Stoner parameter of V for two directions in reciprocal space. Susceptibilities are given in units of $\chi(0)$ (see table 1). The length of the q vector is given in units of $2\pi/a$. ●: χ_0; O: χ; ∇: I. The curves for different directions may be distinguished by the last point on the curve: for the (0,0,1) direction this is $q = 1$; for (1,1,1) direction this is close to 0.9.
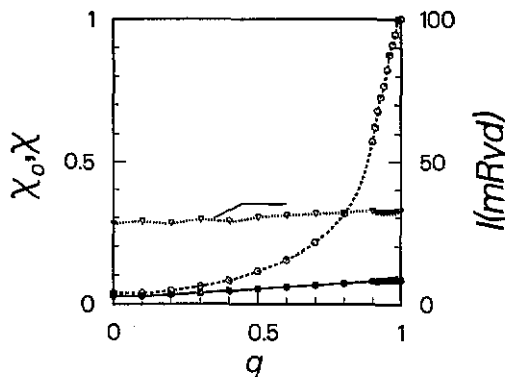

Figure 2. The q dependence of unenhanced and enhanced susceptibilities and of the Stoner parameter of Cr for the (0,0,1) direction. The same symbols are used as in figure 1. Susceptibilities are given in units of the maximum value of enhanced susceptibility, χ_{max}. Here $\chi_{max} = 8.03 \times 10^{-4}$ emu/mole.

of the wave vector q are shown in figures 1–4 (and in figures 6–10).

Below we will deal with the results for the non-magnetic and the magnetic metals separately. But some remarks on common trends seem in order first.

Firstly, it is seen that the Stoner parameter depends on q only weakly, with the exception of FCC-Co (see below). Secondly as is intuitive, the induced magnetic moment in all cases leads to an effective field that is larger than the applied field and hence to an enhanced susceptibility χ that is larger than the unenhanced χ_0. The real picture is, however, more complicated since self-consistency changes both the spin-density and the charge-density, in the latter case that of all electrons including the core electrons. In particular, for ferromagnetic FCC-Co we obtain the surprising result that the unenhanced and the enhanced susceptibilities are practically equal for small q. We emphasize that this does not mean that the first response given by the unenhanced susceptibility leads to a self-consistent state. Rather, for full
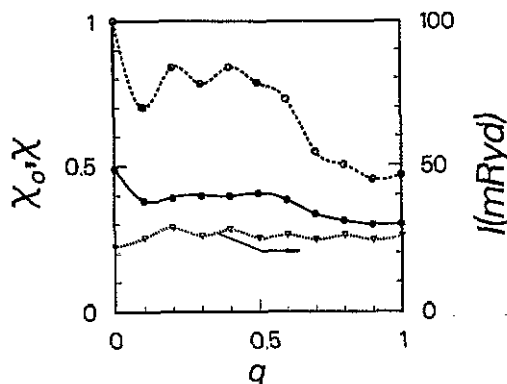
Figure 3. The q dependence of unenhanced and enhanced susceptibilities and of the Stoner parameter of Rh for the $(0,0,1)$ direction. The same units and the same symbols are used as in figure 1. The value of χ_{max} is given in table 1.
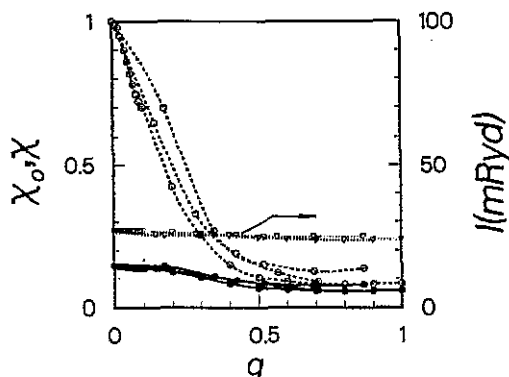

Figure 4. The q dependence of unenhanced and enhanced susceptibilities and of the Stoner parameter of Pd for three directions in reciprocal space. The same units and the same symbols are used as in figure 1. The curves for different directions may be distinguished by the last point on the curve: for the $(0,0,1)$ direction this is $q = 1$, for the $(1,1,1)$ direction this is close to $q = 0.9$ and for the $(1,1,0)$-direction this is close to 0.7. The value of χ_{max} is given in table 1.

self-consistency, a number of further iterations is needed which do not increase the magnetic moment. Thirdly, as functions of q, the two susceptibilities have common trends: weak extrema in χ_0 show up as pronounced extrema in χ, and, in most cases, where one is convex (concave) the other is too.

3.1. Non-magnetic V, Cr, Rh and Pd

Figures 2 and 4 show that the susceptibility enhancement is strong for the cases of Cr and Pd. For Cr the maximum of the enhancement corresponds to antiferromagnetic configurations and reaches the value of 12.9 at $q = (0,0,1)$ (in units of $2\pi/a$ throughout). In the case of Pd, the enhancement is maximal for a ferromagnetic configuration ($q = 0$) and reaches the value of 6.85. For other values of q the enhanced χ quickly approaches the unenhanced χ_0.

The situation shown in figures 1 and 3 for V and Rh is different; the enhancement is much weaker and χ is a non-monotonous function of q. In the case of Rh one can

still see a tendency of decreasing enhancement for increasing q, but this is no longer true of V, for which χ has roughly the same value at $q = 0$ and $q = (0, 0, 1)$.

An obvious explanation of the strong enhancement obtained for antiferromagnetic configurations of Cr and a ferromagnetic configuration of Pd is the fact that in these cases magnetic states 'lie nearby'; in fact a rather small increase in the lattice constants in both cases leads to transitions to magnetic states, antiferromagnetic for Cr [33] and ferromagnetic for Pd [34]. The total energy, correspondingly, has a rather flat minimum as a function of the amplitude of the magnetic moment m at $m = 0$, which, because of (13), leads to large values of the magnetic susceptibility.

This is different in the case of Rh where a quasistable ferromagnetic state is found for very large atomic volumes [35], whereas in V ferro- and antiferromagnetic states seem to coexist [36] for large volumes. This property is obviously correlated with the type of q dependence of the susceptibilities of these metals.

Physically, the susceptibility behaviour described above for Cr and Pd has real implications. Indeed, we know that experimentally Cr [37, 38] is basically antiferromagnetic in its ground state, whereas Pd is characterized by strong spin fluctuations [9] which, on the basis of our results for the susceptibility, most likely possess strong ferromagnetic short-range order.

For Pd and V we now compare our static susceptibility for q parallel to $(0, 0, 1)$ with the results of other authors [4] and [14]. In the case of Pd, the form of our $\chi(q)$ curve is very close to that of [4]. Both calculations give a sharp maximum at $q = 0$, decreasing fast for small q and changing relatively little for large q. The value of the enhancement obtained by [4] is somewhat higher than in our case. However, this is a result of an arbitrary scaling of the unenhanced susceptibility before the integral equation for the enhanced susceptibility is solved, and these values cannot be compared directly. We also note that in [4] the vector q defines a continuous change of the applied field, in contrast to our case in which the fields are supposed to be uniform within each atomic sphere.

It appears that this latter point can explain the substantial quantitative difference between the results obtained for V in our calculations and in [4]. Both calculations give approximately the same values for the susceptibility at $q = 0$ and a non-monotonous behaviour of χ with increasing q. However, the decrease of both susceptibilities, and the enhancement reported in [4] for large q were not obtained in our calculations.

Jarlborg [14], who, like us, used fields uniform within each atomic sphere, carried out calculations of the enhancement for three values of $q = (0, 0, q)$ where $q = 0$, 0.5 and 1. In agreement with our calculations, by comparing the enhancement for $q = 1$ with that for $q = 0$ one recognizes a strong decrease in the case of Pd and a small increase in the case of V. However, our calculations do not confirm the linear q dependence of the enhancement for V and Pd supposed by Jarlborg [14].

To estimate the extent of the anisotropy of the susceptibility and of the exchange parameter, calculations for V and Pd were carried out for different directions in reciprocal space (figures 1 and 4). For both metals we found the parameter I to be almost isotropic, whereas the anisotropy of the susceptibility was quite pronounced. However, in the case of Pd (figure 4), the overall behaviour of the susceptibility, i.e. its sharp maximum at $q = 0$ and its monotonous decrease with increasing q is common for all directions of q. This is different for V (figure 1) where in the $(0, 0, 1)$ direction the susceptibility possesses a maximum at $q = 0$ in contrast to the $(1, 1, 1)$ direction in which the susceptibility is a maximum at the Brillouin-zone boundary.

Above, we briefly commented on the weak q dependence of the Stoner parameter; this suggests that the exchange parameter can indeed be treated as a local atomic property, independent of q, having values in the range of 25 to 30 mRyd for all atoms. This is in good agreement with Himpsel [16] who reached this conclusion on the basis of experimental information about magnetic 3d crystals. From our calculations it appears that this is also so for the non-magnetic 3d and 4d crystals.

The weak dependence of I on q allows us to trace back the strong q dependence of the enhanced susceptibility to the q dependence of the unenhanced susceptibility. For $q = 0$ it is well known that χ_0 is connected with a property of the unperturbed state, namely the density of states at the Fermi energy, because in this case the applied field lifts the spin degeneracy of the bands, leading to a repopulation of the shifted spin-up and spin-down bands at the Fermi energy. For non-vanishing q the situation is substantially more complicated because the change of the electronic structure cannot be reduced merely to shifted states. In the case of Pd we see that the high density of states at the Fermi energy does not lead to a high unenhanced susceptibility for large q. As pointed out in section 2, for $q \neq 0$, states of opposite spin projection are separated by the vector q in reciprocal space and, in general, they hybridize. Bonding states have lower energy and possess a positive spin projection on the local direction of the magnetic field; antibonding states have higher energy and possess a negative spin projection. However, those states close to the Fermi energy in zero field that become antibonding states will be emptied in a finite field. If such states exist in substantial numbers, they will lead to a noticeable increase of the local magnetic moment and to a large unenhanced susceptibility. An example of this is the case of Cr [39] for which there are large ('nesting') pieces of the Fermi surface separated by the vector $q \simeq (0,0,1)$ and, as a result, the susceptibility χ_0 for $q \simeq (0,0,1)$ is of the order of three times higher than it is for $q = 0$.

3.2. Longitudinal susceptibility of Fe, Co and Ni

We now turn to a discussion of our results shown in figures 5–10 which concern the metals BCC-Fe, FCC-Fe, FCC-Co, HCP-Co and FCC-Ni. We emphasize again that we now determine the susceptibilities χ and χ_0, and the Stoner parameter in the magnetic states as described in section 2 and not in non-magnetic states.
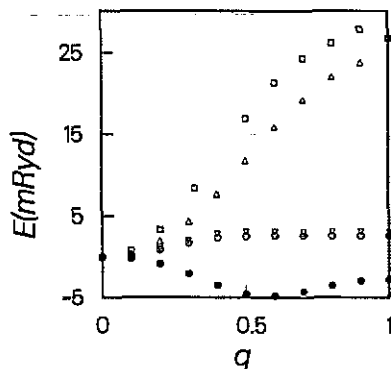

Figure 5. The total energy as a function of q for the (0,0,1) direction. ●: FCC-Fe; Δ: BCC-Fe; ○: FCC-Co; □: HCP-Co; ∇: Ni.
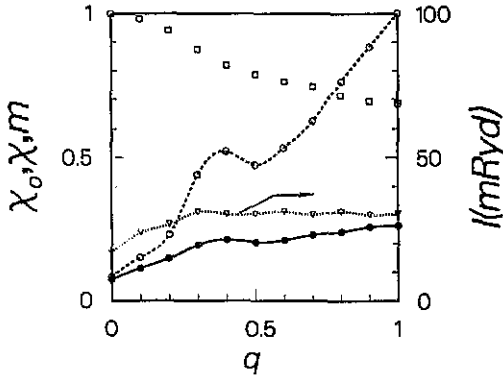
Figure 6. The q dependence of unenhanced and enhanced susceptibilities, of the Stoner parameter and of the local magnetic moment of FCC-Fe for the (0,0,1) direction. The same units and the same symbols are used as in figure 1 for susceptibilities and for the Stoner parameter. □: magnetic moment given in units of $m_0(0)$. Here $\chi_{max} = 2.18 \times 10^{-4}$ emu/mole $m_0(0) = 2.55 \mu_B$.
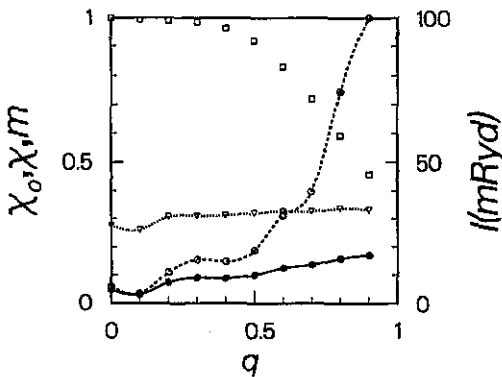

Figure 7. The q dependence of unenhanced and enhanced susceptibilities, of the Stoner parameter and of the local magnetic moment of BCC-Fe for the (0,0,1) direction. The same units and the same symbols are used as in figure 6. Here $\chi_{max} = 3.50 \times 10^{-4}$ emu/mole and $m_0(0) = 2.13 \mu_B$.

We begin with figure 5 which shows the total energy as a function of the wave vector q thus giving information about the state of 'equilibrium' at a given q. For FCC-Fe detailed results have been obtained previously by means of LMTO and ASW calculations [19, 20], Ni and BCC-Fe have also been the objects of previous discussions [32]), but our results for Co are new.

For FCC-Fe the magnetic moment decreases slowly with increasing q, attaining at $q = 1$ about 70% of its maximal value. The total energy of FCC-Fe is minimized for $q = 0.6$. Therefore, in agreement with experiments [40] and previous calculations [19, 20], the ground state of FCC-Fe is non-collinear; however, in the four other cases it is ferromagnetic. For BCC-Fe (figure 7) the magnetic moment is approximately unchanged up to $q = 0.3$ and then decreases for increasing q; the larger q, the faster its decrease. For $q = 1$, different methods give different results [32] for the value of the self-consistent magnetic moment, a fact that is explained by detailed investigations [32]; these showed that for values of q close to one there are two states, magnetic
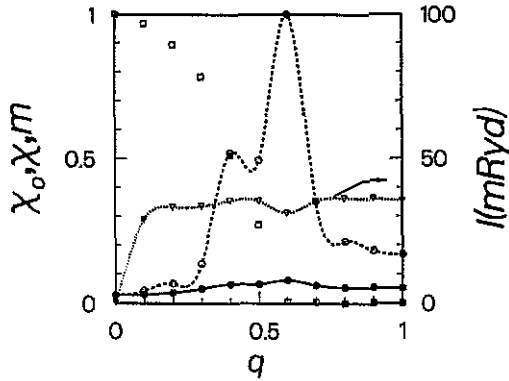
Figure 8. The q dependence of unenhanced and enhanced susceptibilities, of the Stoner parameter and of the local magnetic moment of FCC-Co for the (0,0,1) direction. The same units and the same symbols are used as in figure 6. Here $\chi_{max} = 8.83 \times 10^{-4}$ emu/mole and $m_0(0) = 1.54\mu_B$.
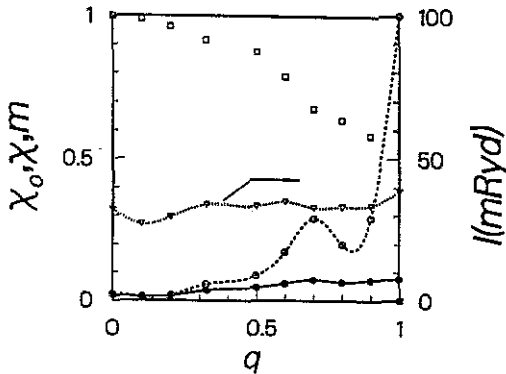

Figure 9. The q dependence of unenhanced and enhanced susceptibilities, of the Stoner parameter and of the local magnetic moment of HCP-Co for the (0,0,1) direction. The same units and the same symbols are used as in figure 6 for susceptibilities, for the parameter I and for the magnetic moment. The value of q is given in units of $2\pi/c$. Here $\chi_{max} = 7.36 \times 10^{-4}$ emu/mole and $m_0(0) = 1.54\mu_B$.

and non-magnetic, for which the difference in the total energy is very small. The value of the self-consistent magnetic moment reacts sensitively to the details of the calculational procedure, the choice of the lattice constant, the basis set etc. Our calculations showed a pronounced instability at $q = 1$ a result which needs further investigation.

For the cases of FCC-Co and Ni we obtain the important result that starting at $q = 0.6$ for Co and $q = 0.5$ for Ni the magnetic moment vanishes, i.e. for large values of q the self-consistent state is non-magnetic. Since the function $m(q)$ contains information about the dependence of the local magnetic moments on the angles between the spins of adjacent atoms, our finding is important for finite-temperature properties of itinerant-electron magnets. In particular, it implies that the assumption that a disordered local moments state exists [41], i.e. that the values of the local moments are independent of the interspin angles, is not valid for FCC-Co and Ni, even for qualitative considerations.
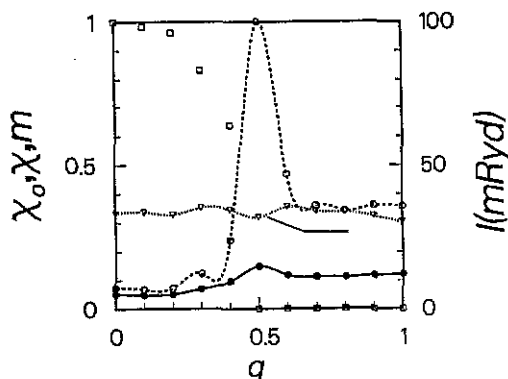
Figure 10. The q dependence of unenhanced and enhanced susceptibilities of the Stoner parameter and of the local magnetic moment of FCC-Ni for the (0,0,1) direction. The same units and the same symbols are used as in figure 6. Here $\chi_{max} = 4.19 \times 10^{-4}$ emu/mole and $m_0(0) = 0.59 \mu_B$.

In the case of HCP-Co the magnetic moment decreases slowly with increasing q, retaining 60% of its ferromagnetic value at $q = 0.9$. However, at $q = 1.0$ the state of lowest energy is non-magnetic.

The non-self-consistent and self-consistent response of the local atomic moments to a small applied field, as well as the values of the exchange parameters, I, are shown in figures 6–10 as functions of q. In all five cases the susceptibility is minimal for the ferromagnetic configuration or for configurations close to it and the values of the enhancements are very small. According to (13), this shows that a given change of the amplitude of the magnetic moment costs more in the ferromagnetic case than in the case of configurations having large q.

If we suppose that a deeper minimum of the total energy of the self-consistent state, $E_q(m_0(q))$, corresponds to a steeper parabola in (13), the minimum of the susceptibility for $q = 0$ may be considered to be a natural result for Co, Ni and BCC-Fe because of the ferromagnetic ground state of these metals. However, FCC-Fe has a non-collinear ground state and, hence, this explanation is not valid for it. We believe, instead, that the following is important: the ferromagnetic 3d metals adjust their Fermi energies in the self-consistent states such that the state densities at the Fermi energy are, in general, low. As a result, the susceptibility is not high, even when the ferromagnetic configuration does not correspond to the minimum of the total energy. For non-collinear states ($q \neq 0$), however, we previously discussed another mechanism that increases the susceptibility by hybridization.

In the cases of FCC-Fe and BCC-Fe the susceptibility has a clear tendency to increase with increasing q. This is quite different for Ni and FCC-Co, for which the enhanced susceptibility has a sharp peak (figures 8 and 10) near those values of q that mark the boundary between the magnetic and non-magnetic states. For HCP-Co (figure 9) the borderline between magnetic and non-magnetic states is close to the Brillouin-zone boundary, and again we have a sharp increase of the enhanced susceptibility here. Thus, near these q values, there are two different self-consistent states with nearly the same total energy giving rise to a very flat minimum of the total energy as a function of the magnetic-moment length, m. Any consistent theory of finite-temperature properties of itinerant-electron magnets must take into account the variation of the energy of the self-consistent state with q (figure 5) as well as

the corresponding variation with local moment size. The large peak in the enhanced susceptibility for Ni and Co close to the boundary between the magnetic and non-magnetic states will result in an important contribution to the partition function of the crystal due to larger statistical weights of these states.

We return now to a discussion of the q dependence of the Stoner parameter, I. It is quite remarkable that in view of the pronounced q dependences of the susceptibilities, the quantity I is as constant as it is, except in the aforementioned case of FCC-Co. In agreement with [14] the values of I for Fe, Co and Ni, for q not too close to 0, have a tendency to be higher than for the other metals considered here.

On the basis of these results we repeat that the Stoner parameter can, for many practical purposes, be treated as a constant characterizing a particular atom. Substantially lower values of I obtained for ferromagnetic configurations of FCC-Fe and FCC-Co show, however, that (10)–(12) fail to describe the connection between unenhanced and enhanced susceptibilities in these cases. We relate this difficulty to the fact that in (10) the effects of a charge density disturbance caused by the magnetic field are neglected. We suggest the following explanation for the fact that this difficulty only occurs for configurations close to ferromagnetic, and for magnetic crystals. In this case, applying a field leads to transitions of some electrons from down-spin states to up-spin states. If there is a large difference between the initial and the final states, the charge distribution may be noticeably disturbed. For Fe and Co the difference of the spin-up and spin-down states at the Fermi energy can be substantial because of the large magnetic moment of the ferromagnetic state and, consequently, the large exchange splitting of the spin-up and spin-down bands. Note that for non-magnetic crystals this splitting is zero and for Ni it is relatively small. None of these difficulties occur for large q, for which there is a strong hybridization of the spin-up and spin-down states. In this case the field will not cause the transition of electrons from occupied states to empty states; it leads, instead, to an increase of the positive spin projection in the bonding states and of the negative projection in the antibonding states, and a sizeable charge-density rearrangement does not take place.

In closing we want to emphasize that there are two ways to introduce the parameter I for a magnetic crystal. In the first case (see, e.g., [30, 42]) the parameter I is considered to be a coefficient of proportionality between the value of the magnetic moment and the value of the corresponding exchange field, where the exchange field characterizes the difference in the potentials experienced by the electrons with opposite spin projections. A perturbation treatment [42] or a simplified variational approach [12, 13] allows an estimate of I based on the electronic structure of non-magnetic states. The value of I so determined serves to investigate the instability of the non-magnetic state.

An alternative way to introduce the parameter I (see, e.g., [7]) is to consider it as a coefficient of proportionality, not between the magnetic moment and the exchange field, but between deviations of these quantities from their equilibrium values. This value of I serves to calculate the enhanced susceptibility of a magnetic crystal and is estimated in the present paper.

If we suppose the magnetic moment and the exchange field are strictly proportional, then both values of I are the same. Our calculations show that this supposition holds for non-collinear magnetic configurations. However, for a ferromagnetic configuration, the parameter I shows, in some cases, 'an instability' which we explain by a charge density variation caused by the change of the magnetic moment. The effect of

this charge transfer depends sensitively on the wave functions of the electron states with energies close to the Fermi level. Therefore, the instability shows up differently for different metals, depending on the lattice structures and even on the lattice spacings. In our calculations, this effect appears to be especially strong for FCC-Co, where a small difference between the enhanced and unenhanced susceptibilities leads to a value of I close to zero.

Note, that in [7] a formula was derived for the exchange parameter of the ferromagnetic state. For Fe and Ni this formula gives results which are very close to the results of our calculations. However, for Co the difference is large. We think that simplifications made in the derivation of the formula are unjustified and do not account for peculiarities of the charge and spin self-consistency of the electronic states of FCC-Co in a magnetic field.

4. Conclusions

We applied *ab initio* electronic-structure calculations to study basic physical pictures, in this case for a number of transition metals that were chosen to demonstrate various different but typical properties. After a brief look at the theoretical basis we concentrated on the unenhanced and the enhanced static but wave-vector dependent, magnetic susceptibilities and the Stoner-exchange parameters for the non-magnetic metals V, Cr, Rh and Pd, and the magnetic metals Fe, Co and Ni, all at zero temperature.

In the first group we contrasted the susceptibility behaviour of Cr (in theoretical equilibrium, with a slightly decreased lattice constant) with that of Pd, on one hand, these being near an antiferromagnetic and a ferromagnetic instability, respectively, with V and Rh, on the other hand, which show no such features. In all these cases the Stoner parameter, $I(q)$, was found to be nearly constant and can therefore be treated as an atomic property.

Our results for the magnetic metals contrasted clearly the two forms of Fe: FCC-Fe having a non-collinear and BCC-Fe a ferromagnetic ground state. For FCC-Co and Ni the self-consistently-determined magnetic moments were found to vanish for values of q larger than 0.6 and 0.5, respectively. This, in our opinion, makes a disordered local moment state, which has repeatedly been postulated [41, 43], highly unlikely in Co and Ni. Furthermore, the large peak in the enhanced susceptibility near the values of q obtained and interpreted by us will carry large statistical weight in the partition function. This must, in our opinion, be taken into account by any theory for finite-temperature properties of itinerant-electron magnets. Finally, the Stoner parameter, $I(q)$, in the magnetic metals, and determined in the magnetic states (and not in the often-used non-magnetic states), was found to be nearly constant for values of q that were not too small. Hence, it can again be treated as an atomic property. However, for q near 0, the ferromagnetic regime, the Stoner parameter calculated shows quite a peculiar behaviour, especially for FCC-Co; a behaviour that we tried to relate to properties of the electronic structure.

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