

Calculation of longitudinal magnetic fluctuations in iron by a Landau energy and force method

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 8647

(<http://iopscience.iop.org/0953-8984/3/44/011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 10:41

Please note that [terms and conditions apply](#).

Calculation of longitudinal magnetic fluctuations in iron by a Landau energy and force method

M U Luchini†‡§, Volker Heine† and G J McMullan†

† Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

‡ Theoretische Physik, ETH-Hönggerberg, CH 8093, Zürich, Switzerland

Received 8 November 1990, in final form 24 May 1991

Abstract. The concept of a Landau energy is used to calculate the energy of magnetic fluctuations. This is used to obtain fictitious magnetic fields akin to the Hellmann–Feynman forces used in phonon calculations. This generalized force method is applied to the spectrum of longitudinal magnetic fluctuations and specific numerical results are presented for Fe.

1. Introduction

The present paper concerns the calculation of longitudinal magnetic fluctuations in itinerant electron magnets and presents specific numerical results for iron. Our method extends previous work and draws together two threads. Firstly the total energy of the fluctuation is cast in the form of a Landau energy i.e., the equivalent at $T = 0$ of the Landau free energy function in the theory of second order phase transitions. Secondly we use the Landau formulation to obtain fictitious magnetic fields akin to the Hellmann–Feynman forces used in the calculation of phonon spectra. Calculating these fields is far easier than evaluating the total energy directly. It is also more accurate by virtue of the usual argument which notes that the ‘forces’ are first order in the ‘displacements’ while the total energy is quadratic. We then use this generalized force method to calculate the spectrum of longitudinal magnetic fluctuations in iron using a realistic parametrization of the full band structure with proper consideration of the s and p electrons. These are known to be important in determining the low-energy properties of iron.

As mentioned above we cast the energy in the form of a $T = 0$ Landau energy function, in our case expanding about the ferromagnetic ground state. In this way one can incorporate terms beyond second order in the amplitude of the fluctuation δm_q which are, of course, given by the longitudinal susceptibility $\chi_{||}(q)$. In modern theories of magnetism there is considerable emphasis on mode–mode coupling which appears as higher order terms in the Landau free energy expansion. Such terms can be calculated directly from the comparison of a number of magnetization configurations. In principle, therefore, we insert into our computational sample of

§ Address from 1st September 1991: Institute for Theoretical Physics, University of California, Santa Barbara, CA 93106, USA.

iron some longitudinal fluctuations involving one or more components δm_q and evaluate the total energy of the configuration, in much the same way as one currently does for phonon frequencies. This approach avoids the problem of basis set convergence in a perturbation evaluation of $\chi(q)$. The perturbation expression involves two summations: one over the few occupied bands and one over the infinite number of unoccupied bands complete with matrix elements between them. The first summation poses no great problems but, in the case of phonon frequencies, the second is notorious for being badly convergent and renders the perturbation method all but unusable (Van Camp *et al* 1983). We believe this could be a problem in the case of longitudinal magnetic fluctuations as well and prefer to avoid a perturbative treatment. Our approach instead focuses directly on the energies and magnetizations of particular configurations.

This work also extends previous ideas on how the computations are both performed and analysed. In principle, one calculates the total energy of the selected configuration and indeed this is the quantity we are principally interested in. However this is rather inefficient. For a phonon, in fact, one calculates the Hellmann-Feynman forces on the atoms i.e., the restoring forces for a given set of displacements and hence the phonon frequencies. This has the advantage that the restoring force depends linearly on the displacement amplitude (as long as the latter is small) while the total energy depends quadratically. A further advantage is that one can obtain far more information from a single calculation of the electronic structure. This is because the restoring forces result from the sum and the interaction of displacements belonging to all harmonics and this fact can be used to obtain information about a large region of the spectrum. By contrast a calculation of the total energy yields just one number pertaining to the particular configuration examined. What is the equivalent of this discussion for longitudinal magnetic fluctuations?

For transverse fluctuations the general answer is already contained in a previous publication (Small and Heine 1984): the magnetic couple acting on a magnetic moment m_j in a non-equilibrium configuration is related to the quantity

$$h_j = \frac{1}{2} \{ \Delta_j - I m_j \}. \quad (1.1)$$

Here Δ_j is the actual exchange splitting inserted into the calculation of the electronic structure, m_j is the resultant magnetic moment on site j and I is the exchange interaction. For transverse magnetic excitations, Δ_j and m_j will generally differ in *direction*, giving rise to a couple on the moment m_j . This difference in direction is expressed in a transferred moment i.e., a moment due to the polarization of the *electron cloud in the environment*. Under these couples the configuration of moments will precess. However, the system would be fully in static equilibrium if at each site we added a set of external magnetic fields which exactly cancelled the local differences between the spin-splitting and the exchange fields. This new set of fields h_j is given by (1.1).

In the present work we will consider all exchange splittings Δ_j in the same z -direction but differing in magnitude from the value

$$\Delta_{\text{FM}} = I m_{\text{FM}} \quad (1.2)$$

of the ferromagnetic ground state. In section 2 we shall discuss in detail how one formulates the energy of such a non-equilibrium structure correctly. It turns out that

to maintain a value of the magnetization greater (or smaller) than the ferromagnetic one, it is again necessary to impose upon the system a set of fictitious magnetic fields. These are exactly the same fields as those we considered in (1.1) and can be related to the Landau free energy function for a longitudinal fluctuation. The crucial step consists of comparing the Landau energy for a *non-equilibrium* configuration in the absence of external fields with the total energy of an *equilibrium* configuration under the set of external fields $\{h_j\}$.

The model for the electronic structure and the computational method follows previous work (Luchini and Heine 1989). We believe it is important to include fully the effect of the s and p electrons in the calculations if one wants to obtain quantitative comparisons with experiment. The magnetic properties, in particular the low-energy region of the spectrum, are notoriously sensitive to the details of the electronic structure. In particular we can quote the substantial differences which have been obtained in various calculations of the spin wave stiffness of iron (Wakoh *et al* 1971, Wang *et al* 1982, Muniz *et al* 1985, Luchini and Heine 1989). We will mostly be interested in the longitudinal stiffness but there is every reason to expect that the same instability is present. In Fe hybridization between d and sp electrons seems to be of paramount importance in determining the low q behaviour.

The calculations we have performed employ the recursion method (Haydock 1980) to calculate the local moments and, in some cases, the total energies of longitudinal magnetization waves. Though the essential magnetic interactions are confined to the relatively narrow d band, the large overall bandwidth which results from the inclusion of the sp electrons leads to extra numerical problems. These have been already been discussed in detail (Luchini and Heine 1989) and in section 4 we limit ourselves to sketching briefly their solution. However there are two important aspects of the configurations we are considering here which were absent in those which have been previously published. We will be examining fluctuations around the the ferromagnetic ground state and it is crucial that the self-consistent solution be identified with the minimum of the total energy not only in principle but also numerically. This is the magnetic analogue of a familiar problem encountered, for instance, in the relaxation of surfaces and defects, where it is crucial that the minimum of the total energy correspond to the solution that has no net forces on any site. In section 4 a formulation of the problem which ensures that this is always the case is discussed (Luchini and Nex 1990).

The other important aspect is the fact that calculating the energy of these configurations involves a consideration of the Coulomb terms in the Hamiltonian. There are two questions to be considered here. One is the approximation used to account for charge transfer or, in other words, the value of the Coulomb U that one assumes. The other is the precise formulation of the energy that includes such charge transfers. The latter problem turns out to be solved by the so-called bond energy of Sutton *et al* (1988). For the former problem, the most common approximations ($U = 0$ and $U = \infty$) are used, and the results compared.

The actual computational problem to which the Landau formulation will be applied is the calculation of the energy spectrum of longitudinal fluctuations around the ferromagnetic ground state in iron. This was prompted by the success of a recent model of itinerant ferromagnets (Lonzarich and Taillefer 1985) in which longitudinal fluctuations play an important role. The model of Lonzarich and Taillefer was specifically designed for weak ferromagnets and its first applications were confined to Ni_3Al and MnSi . The principal innovation of this model is the inclusion of the

corrections to Stoner theory arising from enhanced spin fluctuations. It takes into account both transverse and longitudinal modes and their quantum dynamics. Here we are interested in investigating its applicability to the case of stronger ferromagnets like iron. In these terms we wish to focus on the importance or otherwise of the contributions of the longitudinal modes to the thermodynamics.

The model relies on four independent parameters, which can all, in principle, be determined either from electronic structure calculations or from fitting to experimental data. The first two parameters, a and b , arise from the Taylor expansion of the free energy as a function of magnetization:

$$F(M) = F(0) + \frac{a}{2}M^2 + \frac{b}{4}M^4 + \dots \quad (1.3)$$

The range of validity of the truncation of this expansion is the first issue our calculations address. Figure 1 shows a plot of the total energy, as defined in section 2, against magnetization for our computations on iron. Here the magnetization varies only in magnitude and is the same over the whole cluster. The total energy is calculated *ab initio* from the electronic structure. Indeed we verify that equation (1.3) applies remarkably well over a wide range of M . It is comforting that this curve is very similar to that obtained earlier by Schwarz and Mohn (1984) using the fixed spin-moment method and a different band structure.

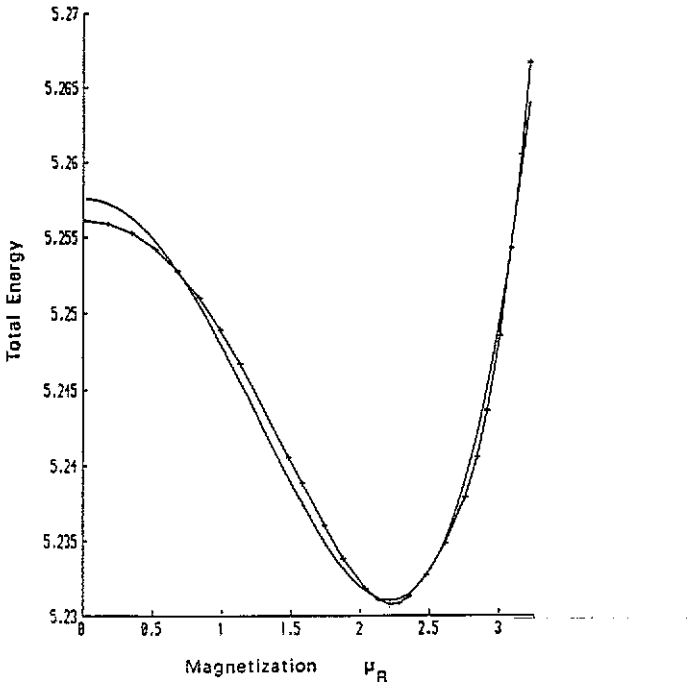


Figure 1. Plot of total energy as a function of magnetization. The points are joined as a guide to the eye. A fit to the form $E_0 + aM^2 + bM^4$ as described in the text, is superimposed.

The third parameter in the model is the sum of two separate contributions, the transverse and longitudinal stiffnesses, c_{\parallel} and c_{\perp} . These become equal to each

other in a cubic lattice for a weak ferromagnet in the limit of small M , which is not our case. In fact c_{\perp} is directly related to the spin wave stiffness. This has already been calculated for the present parametrization of the electronic structure and found to be in excellent agreement with experiment (Luchini and Heine 1989). The longitudinal stiffness c_{\parallel} has not been calculated before for Fe. We will consider a set of configurations which have a sinusoidal modulation of the magnetization at a single q around the ferromagnetic ground state. The energy of such configurations should be proportional to $c_{\parallel} q^2 M_q^2$ so that,

$$\chi_{\parallel}^{-1}(q) = \chi_{\parallel}^{-1} + c_{\parallel} q^2. \quad (1.4)$$

A calculation of the energies of such configurations would enable one to obtain c_{\parallel} directly. Finally the fourth parameter γ is related to the differential scattering cross-section for inelastic neutron scattering. Its variation in a wide class of magnetic materials is quite small and since additionally T_c depends on $\gamma^{1/4}$ its precise numerical value is not very important.

In section 2 we consider the general problem of calculating the energy of a non-equilibrium structure and derive our Landau formulation of the energy of magnetic fluctuations on which we base the rest of our work. Using it in section 3 we show how the sets of fictitious fields $\{h_j\}$ and local moments $\{m_j\}$ can be used to obtain the total energy of an arbitrary fluctuation. In section 4 we briefly consider the problem of obtaining a self-consistent solution for the total energy which coincides with a configuration with net zero forces on all sites and, in more detail, the question of charge transfer. Finally section 5 contains our detailed numerical results.

2. Definition of the Landau energy

Traditionally electronic structure calculations of solids have been mainly concerned with *ground state* energies. Density functional theory in particular has been very successful at predicting ground state energies and has spawned a large variety of total energy methods. However here we are concerned with *non-equilibrium* configurations, in particular longitudinal magnetization fluctuations. The definition of the energy of such a fluctuation is a more general problem. Its resolution is therefore more important than the details of the particular calculation at hand.

One approach that has been used in the past relies on the functional integral formulation (Hubbard 1979). However even in the static approximation this approach is plagued with ambiguities. These arise from the fact that it is possible to resolve the electron interactions, in our language the interactions of the exchange fields Δ_j , into a quadratic form in more than one way. Different decompositions lead to different results after the static approximation is used (Hubbard 1979). The standard approach leads to a term $\Delta^2/4I$ being added to the one-electron energy. This is different from our result and in the light of the ambiguities of the formalism we shall spell out our definition of the energy with a care that may appear at first sight as pedantic.

It seems best to follow the idea of the Landau free energy in the context of the theory of second order phase transitions. In this field one also is concerned with defining the energy of non-equilibrium states. Specifically one considers an order parameter x , say, and asks what would be the value of the free energy of the system as a function of x .

In order to state the ideas at their clearest and simplest we first consider a simple elastic system at $T = 0$ where one atom may have a displacement x . We will consider in detail the magnetic case later. The Landau energy $U_L(x)$ would be given by

$$U_L(x) = U_0 + \frac{1}{2}\lambda x^2 \quad (2.1)$$

where λ is the force constant. The problem consists in defining this operationally since simply postulating some non-zero x does not correspond by itself to any realisable state. The solution, as we hinted earlier, consists in applying a suitable external force F which brings the state into equilibrium. The energy of the whole system is then given by

$$U(F) = U_L(x) - Fx \quad (2.2a)$$

$$= U_0 + \frac{1}{2}\lambda x^2 - Fx. \quad (2.2b)$$

This has to be minimised with respect to x to give correctly

$$F = \lambda x. \quad (2.3)$$

Conversely, we can define $U_L(x)$ by

$$U_L(x) = U(F) - (-Fx). \quad (2.4)$$

This procedure affords the following interpretation. We apply a force F to give the required displacement x for an *equilibrium* system whose energy $U(F)$ we can define and calculate by conventional methods, precisely because it is in equilibrium. Then $U_L(x)$ as defined by equation (2.4) is the internal energy of the system corresponding to that value of x i.e., $U(F)$ with the potential energy $-Fx$ of the external force subtracted out. This is really a restatement of equation (2.2a).

Turning now to our magnetic system, in practice, we postulate a set of exchange splittings Δ_j in the one-electron equations. The electronic structure in the presence of the exchange fields Δ_j is then calculated and the local moments m_j obtained. Let us start by specifying the Hamiltonian for the whole system. In this we follow the usual formulation of the problem discussed in detail in You and Heine (1982).

$$H_{\text{total}} = H_{\text{band}} + H_{\text{int}} \quad (2.5)$$

$$H_{\text{band}} = \sum_{jj'l'l'} h(j, l, j', l') c_{jl}^\dagger c_{j'l'} + HC \quad (2.6)$$

$$H_{\text{int}} = -\frac{1}{4} \sum_j I \widehat{m}_j^2 \quad (2.7)$$

where H_{band} is the purely tight-binding, non-magnetic hopping Hamiltonian between orbital l on site j and orbital l' on site j' and \widehat{m}_j is the magnetic moment operator. In practice this is solved by the one-electron Hamiltonian

$$H_{1\text{-elec}} = H_{\text{band}} + H_{\text{ex}} \quad (2.8)$$

$$H_{\text{ex}} = \sum_j -\frac{1}{2} \Delta_j \cdot \sigma_j \quad (2.9)$$

where Δ_j is the exchange splitting (or $\Delta_j/2$ the exchange potential) on atom j and σ_j is the vector of Pauli spin matrices ($\sigma_x, \sigma_y, \sigma_z$) on atom j . The procedure now consists in calculating the one-electron energies ϵ_n of the one-electron Hamiltonian (2.8) and filling up the bands to a common Fermi level E_F determined by the total number of electrons.

To calculate the ground state we impose self-consistency on $\Delta_j = Im_j$ where the local moment m_j is properly given by

$$m_j = \langle \Psi | \widehat{m}_j | \Psi \rangle \tag{2.10}$$

$$= \langle \Psi | \widehat{n}_{j\uparrow} - \widehat{n}_{j\downarrow} | \Psi \rangle \tag{2.11}$$

with the respect to the Slater determinant of the one-electron solutions Ψ . This procedure is usually considered as the Hartree-Fock solution to the original many-body problem. However this is not the only way of viewing it. A more modern interpretation based on density functional theory is discussed in Stollhoff *et al* (1990) where (2.7) plays the rôle of the exchange and correlation energy functional.

We next consider the equilibrium system in the presence of the external fields h_j applied individually to the atoms j .

$$H'_{\text{total}} = H_{\text{band}} + H_{\text{int}} + H_{\text{ext}} \tag{2.12}$$

$$H_{\text{ext}} = - \sum_j h_j \cdot \widehat{m}_j \tag{2.13}$$

$$h_j = \frac{1}{2}(\Delta_j - Im_j). \tag{2.14a}$$

We assert that our solutions of $H_{1\text{-elec}}$, combined into the whole Slater determinant Ψ , then give the correct self-consistent solution of the whole system in the set of external fields $\{h_j\}$. The reason is that we can turn equation (2.14a) around to write the total exchange splitting

$$\Delta_j = Im_j + 2h_j \tag{2.14b}$$

as the sum of the internal (Im_j) and external ($2h_j$) contributions. For this to be true we now have to make Δ_j self consistent as in equation (2.14b). (The factor of two in equations (2.14a,b) arises from the fact that the energy of a moment in a field $-h \cdot \sigma$ gives a full splitting of $2h\sigma$.)

Conversely if we solve the one-electron equations for some arbitrarily inserted splitting Δ_j , then the solutions (combined into a total Slater determinant Ψ) give the correct self-consistent equilibrium state of the system in the set of external fields given by equation (2.14a). We can therefore define the corresponding Landau energy $U_L(m_j)$ in analogy with equation (2.4) as follows

$$U_L(m_j) = \langle \Psi | H'_{\text{total}} | \Psi \rangle - \langle \Psi | H_{\text{ext}} | \Psi \rangle \tag{2.15a}$$

$$= \langle \Psi | H_{\text{band}} + H_{\text{int}} | \Psi \rangle \tag{2.15b}$$

$$= \langle \Psi | H_{\text{band}} + H_{\text{ex}} | \Psi \rangle + \langle \Psi | H_{\text{int}} - H_{\text{ex}} | \Psi \rangle \tag{2.15c}$$

$$= U_{1\text{-elec}} + \sum_j \frac{1}{2} \Delta_j \cdot m_j - \sum_j \frac{1}{4} Im_j^2. \tag{2.15d}$$

where $U_{1-\text{elec}}$ is the sum of the one-electron eigenvalues ϵ_n , or in practice

$$U_{1-\text{elec}} = \sum_j \int_{-\infty}^{E_F} E n_j(E) dE. \quad (2.16)$$

This form of the Landau energy is precisely what we require since it is a function of m_j only: h_j has disappeared as seen in equation (2.15a) and Δ_j is just an auxiliary variable which cancels out as seen in equation (2.15c).

3. Expansion of the Landau energy

The Landau energy is clearly a very convenient description of a system away from equilibrium. As discussed in section 1, the fields h_j contain information in addition to the total energy and we wish to make use of this in calculating the Landau energy expression.

So how do we relate h_j to $U_L(m_j)$? We consider the system in a set of external fields h_j and write for its energy in analogy with (2.2a)

$$U = U_L(m_j) - \sum_j h_j \cdot m_j. \quad (3.1)$$

The equilibrium values of $\{m_j\}$ are then determined by

$$\left(\frac{\partial U}{\partial m_j} \right)_{h_j} = 0 \quad (3.2)$$

or

$$h_j = \left(\frac{\partial U_L(m_j)}{\partial m_j} \right)_{m_k \text{ for } k \neq j} \quad (3.3)$$

These are the magnetic analogues of the Hellmann-Feynman forces.

By way of illustration of the general method let us examine the simplest case, that of a small uniform change in magnetization. We consider the Taylor expansion of the Landau energy about the ferromagnetic ground state

$$U_L(m_{\text{FM}} + \delta m) = U_{\text{FM}} + \frac{\alpha}{2!} \delta m^2 + \frac{\beta}{3!} \delta m^3 + \frac{\gamma}{4!} \delta m^4 + \dots \quad (3.4)$$

so that

$$h = \frac{\partial U}{\partial m} = \alpha \delta m + \frac{\beta}{2!} \delta m^2 + \frac{\gamma}{3!} \delta m^3 + \dots \quad (3.5)$$

From a particular calculation we obtain both a value of m and of h . To evaluate the three coefficients (α, β, γ) requires three calculations using (3.5), but four calculations using (3.4). Moreover the latter requires subtracting energies which differ by small quadratic terms in δm .

In this work we will only be interested in longitudinal deviations from the ferromagnetic ground state. We drop the vector nature of the local moments and just consider

$$m_j = m_{\text{FM}} + \delta m_j \tag{3.6}$$

so that equation (3.3) becomes

$$h_j = \left(\frac{\partial U_L}{\partial \delta m_j} \right)_{\delta m_k \text{ for } k \neq j} \tag{3.7}$$

We extend our treatment to arbitrary configurations by writing

$$\delta m_l = \sum_{\text{all } q} \delta m_q e^{iq \cdot l} \tag{3.8}$$

where δm_q are complex Fourier coefficients. We expand the Landau energy of the system comprising N atoms to third order in δm_l and use equation (3.8)

$$U_L^{\text{Total}}(\delta m_l) = N U_{\text{FM}} + N \sum_q \sum_{q'} A_{qq'} \delta m_q \delta m_{-q} \delta(q + q' - g) + N \sum_q \sum_{q'} \sum_{q''} B_{qq'q''} \delta m_q \delta m_{q'} \delta m_{q''} \delta(q + q' + q'' - g) + \dots \tag{3.9}$$

The mode-mode coupling coefficients, $A_{qq'}$ and $B_{qq'q''}$, must become equal to the coefficients of the energy expansion per atom for a uniform magnetization in the limit $q \rightarrow 0$ i.e., α and β in equation (3.4).

Consider a particular modulation with wave vector Q

$$\delta m_j = \delta m_0 + \delta m_1 (e^{iQ \cdot l} + e^{-iQ \cdot l}) + \delta m_2 (e^{i2Q \cdot l} + e^{-i2Q \cdot l}) \tag{3.10}$$

where $\delta m_0, \delta m_1$ and δm_2 are real. Our final result for the energy is

$$U_L(\delta m_l) = U_{\text{FM}} + A_{00}(\delta m_0)^2 + 2A_{11}(\delta m_1)^2 + 2A_{22}(\delta m_2)^2 + B_{000}(\delta m_0)^3 + 6B_{011}\delta m_0(\delta m_1)^2 + 6B_{022}\delta m_0(\delta m_2)^2 + 6B_{211}(\delta m_1)^2\delta m_2 + \dots \tag{3.11}$$

where the multiplicities 2 and 6 arise from the different ways in which q, q' and q'' can be chosen as 0, $\pm Q$ and $\pm 2Q$.

We now turn to the evaluation of the fields h_j defined by equations (3.7) using the general form for U_L in (3.9).

$$h_l = \sum_q A_{q,-q} \left\{ \frac{\partial \delta m_q}{\partial \delta m_l} \delta m_{-q} + \delta m_q \frac{\partial \delta m_{-q}}{\partial \delta m_l} \right\} + \sum_{qq'q''} B_{qq'q''} \left\{ \frac{\partial \delta m_q}{\partial \delta m_l} \delta m_{q'} \delta m_{q''} + \delta m_q \frac{\partial \delta m_{q'}}{\partial \delta m_l} \delta m_{q''} + \delta m_q \delta m_{q'} \frac{\partial \delta m_{q''}}{\partial \delta m_l} \right\} \delta(q + q' + q'' - g) + \dots \tag{3.12}$$

Using the inverse transform

$$\delta m_q = \frac{1}{N} \sum_l \delta m_l e^{-iq \cdot l} \quad (3.13)$$

we can perform the differentiations and obtain for our configuration of wave vector Q (3.10)

$$\begin{aligned} h_l &= \frac{1}{N} \sum_q A_{qq} \left\{ \delta m_q^* e^{-iQ \cdot l} + \delta m_q e^{iQ \cdot l} \right\} + \dots \\ &= \frac{1}{N} \left\{ 2A_{00} \delta m_0 + 2A_{11} (\delta m_{-1} e^{-iQ \cdot l} + \delta m_1 e^{iQ \cdot l}) \right. \\ &\quad \left. + 2A_{22} (\delta m_{-2} e^{-i2Q \cdot l} + \delta m_2 e^{i2Q \cdot l}) + \dots \right\} \\ &= 2A_{00} \delta m_0 + 4A_{11} (\delta m_1)^2 \cos Ql + 4A_{22} (\delta m_2)^2 \cos 2Ql \\ &\quad + 3B_{000} (\delta m_0)^2 + 6B_{011} (\delta m_1)^2 + 6B_{022} (\delta m_2)^2 \\ &\quad + 12B_{011} \delta m_0 \delta m_1 \cos Ql + 12B_{211} \delta m_1 \delta m_2 \cos Ql \\ &\quad + 12B_{022} \delta m_0 \delta m_2 \cos 2Ql + 6B_{211} (\delta m_1)^2 \cos 2Ql + \dots \quad (3.14) \end{aligned}$$

We compare with the Fourier expansion of the fields h_l

$$h_l = \frac{1}{N} \sum_q h_q e^{-iq \cdot l} \quad (3.15)$$

Under the same conditions of even configurations this yields our final equations

$$h_0 = 2A_{00} \delta m_0 + 3B_{000} (\delta m_0)^2 + 6B_{011} (\delta m_1)^2 + 6B_{022} (\delta m_2)^2 \quad (3.16a)$$

$$h_1 = 2A_{11} \delta m_1 + 6B_{011} \delta m_0 \delta m_1 + 6B_{211} \delta m_1 \delta m_2 \quad (3.16b)$$

$$h_2 = 2A_{22} \delta m_2 + 6B_{022} \delta m_0 \delta m_2 + 6B_{211} (\delta m_1)^2 \quad (3.16c)$$

where the fields h_j for our configuration (3.10) are given by

$$h_j = h_0 + h_1 2 \cos Ql + h_2 2 \cos 2Ql. \quad (3.17)$$

By a series of calculations on configurations with a range of δm_q one can fit the Fourier coefficients of the fields and those of the moments and obtain all mode-mode coupling coefficients which can be substituted into equation (3.14) to give the Landau energy.

4. Computational details

The physical picture of itinerant electron magnetism on which our model is based is essentially the same as that of You and Heine (1982). This was improved by Luchini and Heine (1989) in the context of spiraling spin configurations in Fe who properly included the s and p electrons in a realistic band structure. Here we very briefly

summarize the physical justification and numerical implementation of the model while referring the reader to the more exhaustive discussions in the aforementioned papers.

We start with a non-magnetic band structure and then impose splittings $\pm\Delta_{jl}$ for each atomic orbital l and each site j in the one-electron equations. Thus electrons in the solid will polarize in the direction of $\pm\Delta_j$'s. For the configurations we consider in this work i.e., longitudinal perturbations around the ferromagnetic ground state, all Δ_j will be parallel and in the ferromagnetic direction, though our model can be used to investigate arbitrary configurations of moments (Small and Heine 1984). We then solve the one-electron equations for Hamiltonian (2.5) to obtain the moments m_j and insert them into (3.16) to define the fields h_j .

For the band structure we employ an spd tight-binding parametrization of Wood's (1962) APW non-magnetic calculation in terms of the usual tight-binding formulation (Slater and Koster 1954). This is known to give a good value for the spin wave stiffness which is notoriously sensitive to the spd mixing (see Muniz *et al* (1985) for a k -space calculation and Luchini and Heine (1989) using recursion.) The crucial step in the calculation consists in deciding the form of the matrix $I_{ll'}$. First principles spin-polarized calculations indicate that the spin-splitting of s- and p-like states is very small compared to that of the d-states (Fritsche *et al* 1987). Moreover the calculations of Cooke *et al* (1980) indicated that there is very little difference between the splittings for d electrons of the t_{2g} and e_g symmetry. Hence we take (Luchini and Heine 1989)

$$\begin{aligned} I_{ll'} &= I = 67 \text{ mRyd} && \text{amongst the d electrons} \\ I_{ll'} &= 0 && \text{otherwise} \end{aligned}$$

where the symbol l includes the azimuthal quantum number. This also provides us with the simplest computational procedure. We take $\Delta_d = 0.1427 \text{ Ryd}$ resulting in $m = 2.125 \mu_B$ for the total moment of the ferromagnetic ground state.

The local densities of states are the central quantities of our calculation and are obtained using the recursion method (Haydock 1980). Computationally the crux of the problem lies in the shape of the density of states which consists of a set of narrow d band peaks with considerable weight on top of a broad, roughly featureless sp band with little weight. The total bandwidth is much larger than that of a pure d band ($\sim 2 \text{ Ryd}$ vs $\sim 0.45 \text{ Ryd}$) so that to obtain adequate resolution in the crucial region of the d bands one needs a correspondingly larger number of levels in the continued fraction, specifically around 90. For reasons of accuracy and stability given in Luchini and Heine (1989) where the computational aspect is discussed in greater detail, we analyse the recursion coefficients obtained from fairly large clusters (~ 1000 atoms) using Gaussian quadrature (Nex 1978, 1984).

Here we only want to discuss briefly the problem mentioned in section 1 of ensuring that computationally the minimum of the total energy corresponds to the self-consistent solution for the moment as it does theoretically. This does not turn out to be so in the quadrature approach unless one is careful about the various quantities computed. The problem lies particularly in the evaluation of the integral in $U_{1-\text{elec}}$

$$\int_{-\infty}^{E_F} E n(E) dE. \tag{4.1}$$

Conventionally this has always been calculated using $n(E)$ as obtained through quadrature but then we find that the minimum does *not* correspond to the self-consistent solution $\Delta = Im$. In proving that the minimum of the total energy is

given by the self-consistency condition one has to perform the integration by parts of $U_{1-\text{elec}}$. This is what causes the problem since the quadrature approximation does not guarantee to preserve the analytic relation between quantities related by differentiation (Nex 1978). The correct procedure is to perform the integration by parts analytically and to consider

$$U_{1-\text{elec}} = E_F \int_{-\infty}^{E_F} n(E) dE - \int_{-\infty}^{E_F} \left\{ \int_{-\infty}^E n(E') dE' \right\} dE. \quad (4.2)$$

In this way both the energy and the moments are all evaluated in terms of the same quantity, the integrated density of states,

$$N(E) = \int_{-\infty}^E n(E') dE' \quad (4.3)$$

and hence no inconsistency can arise. This problem and its solution are fully analysed in Luchini and Nex (1990) where the best numerical implementation which we use in the next section is also given. This problem fully drives home the general point that if one requires an *analytical* relation between various quantities then one must ensure that this analyticity is preserved in the numerical formulation to arbitrary precision.

Let us now turn our attention to the problem of charge self-consistency. Since there are several sites which are not equivalent in a longitudinal fluctuation, the different Δ_j will cause electrons to want to flow between the sites. This charge flow will set up electrostatic potentials between the sites and the system reaches equilibrium when the electrostatic potentials balance the electrostatic energy of the charge flow.

There are two problems to be considered here. The first concerns the value of the Coulomb U that one chooses to insert into the Hamiltonian. Three different approximations have been used. It has been argued that the most appropriate for metals is $U = \infty$ essentially because the value of U is known to be larger than the exchange splitting Δ . In other words, perfect screening dominates. Every site has the same number of electrons, charge transfer being inhibited by the infinite value of U . Alternatively one can insert a value of U derived from experiment and carry out a self-consistency between the charge transfers and the electrostatic potentials. The last approach is to set $U = 0$ and allow free charge flow. This is more appropriate in semiconductors.

Calculations comparing $U = \infty$ and $U = 0$ for magnetic configurations in Fe similar to the ones considered here (Hubbard 1979) showed a substantial difference in the total energy between the two approximations. However those calculations were carried out with a d-band-only model (in fact a one band model fitted to d-band parameters) and it is clear that on-site intra-band transfer can largely compensate for the different exchange splittings without leading to charge flow.

The second problem concerns the correct formulation of the total energy in a system where charge transfer can occur. This has recently been carefully examined by Sutton *et al* (1988) who distinguished between the *band* energy and the *bond* energy. In their formulation these names are a natural choice. The precise procedure consists of deciding on a value of U , inserting a set of energy shifts a_i on each site i and then imposing self-consistency using

$$a_i = U c_i \quad (4.4)$$

where c_i is the amount of charge transfer on site i .

Sutton *et al* showed that in a tight-binding calculation, the correct energy to take is the bond energy. In particular they showed that, in such a calculation, the bond energy is *exact to first order* in the potential shifts. They defined the *bond* energy as

$$U_{\text{bond}} = \int_{-\infty}^{E_F} (E - a_i)n(E) dE \quad (4.5)$$

and contrasted it with the conventional *band* energy

$$U_{\text{band}} = \int_{-\infty}^{E_F} En(E) dE. \quad (4.6)$$

The full derivation of this result is given in detail in their paper. Here we will just indicate how this result comes about and why it is relevant to our calculations.

Let us consider the standard expression for the total energy of a solid in the Hartree approximation. This neglects the exchange and correlation term, which is treated properly in Sutton *et al*, but which does not affect the result.

$$U_{\text{Total}} = \sum_n \epsilon_n + U_{\text{ion-ion}} + U_{\text{double-counting}} \quad (4.7)$$

Let the equilibrium charge density be perturbed as follows

$$\rho \rightarrow \rho + \delta\rho. \quad (4.8)$$

The new one-electron energy is given by

$$\sum_n \epsilon_n = \sum_n \langle \psi_n | \rho_n + \delta\rho_n | \psi_n \rangle \quad (4.9)$$

for the wavefunctions ψ_n , so that the change in the one-electron energy to first order is

$$\delta\epsilon_n = \sum_n \langle \psi_n | \delta\rho_n | \psi_n \rangle \quad (4.10a)$$

$$= \rho_n \delta\rho_n. \quad (4.10b)$$

Let us now consider the double counting term which has the form, after the perturbation

$$-\frac{1}{2} \iint (\rho_n + \delta\rho_n)^2 \quad (4.11)$$

so that the change in the energy due to double counting to first order in the density perturbation is given by

$$-\frac{1}{2} 2\rho_n \delta\rho_n. \quad (4.12)$$

This exactly cancels, to first order, the change in the one-electron energy.

In tight-binding theory normally, one only explicitly computes the sum of the one-electron energies, the band energy (4.6) in this notation. The other terms in the total energy are usually absorbed in some semi-empirical potential V^{eff} . In our calculations this is never written down because it is assumed constant and we only add the extra magnetic terms. However when doing calculations with defect relaxations this semi-empirical potential is very important and it is in this context that Sutton *et al* discuss the problem.

The reason that this discussion applies to our problem is that the semi-empirical potential we assume is constant. This implies that the *first order cancellation of the single particle energy and the double counting term is not included* in our formulation. This is clearly irrelevant when potential shifts are not present but becomes crucial when they are. Clearly calculating the band energy (4.6) will give the wrong answer. However if we calculate the bond energy (4.5) the exact cancellation will be included because we take out the shifts explicitly from the total energy. Since we are only interested in relative energies this is the correct procedure.

As mentioned earlier we will carry out the calculations using both the $U = \infty$ and the $U = 0$ approximation. We will also calculate the total energy in a third approximation called the *local Fermi energy* approximation. In this last approach we impose local charge neutrality but do not have an overall Fermi energy i.e., we allow the system to have little fluctuations in the local chemical potential. It differs from the $U = \infty$ approximation by the amount of overlap between the wavefunctions on neighbouring sites. If local charge neutrality is important we would expect the local Fermi energy procedure to give a good estimate for the energy of the system with $U = \infty$. The last reason for calculating this energy is that the differences in the local Fermi energy from the Fermi energy of the reference ferromagnetic state give a very good estimate of the charge shifts required and substantially cut down the amount of self-consistency loops that one needs.

Finally there are two last small difficulties concerning the charge self-consistency procedure which deserve mentioning. The first concerns the choice of the Fermi energy. Since the bond energy is clearly invariant with respect to the choice of the zero energy point the simplest procedure consists of fixing the Fermi energy at the ferromagnetic value and letting the charge shifts take care of themselves during the self-consistency. This is correct in principle but disastrous computationally. The system is not symmetrical in perturbations around the ferromagnetic energy and this leads during the self-consistency to a loss of total charge neutrality. This easily outweighs the energy of the magnetization fluctuations we seek. The system does eventually converge to the correct answer but for the simplest case ($q = \pi/2$) takes over fifteen iterations. This makes the evaluation of longer wavelength configurations impossible.

The correct procedure is to evaluate the Fermi energy for the configuration at every step in the iteration. In this way total charge neutrality is ensured and because the bond energy is invariant under this procedure the same results as above are obtained. The charge self-consistency typically takes about three iterations. Since we are considering configurations with a given amplitude we must also carry out a self-consistency in the moments. It is best to do these two separately, imposing self-consistency first on the magnetization configuration that is required and secondly on the potential shifts to obtain local charge neutrality, and then back to the moments until convergence on both sets of variables is achieved. At each step the variables that one is making self-consistent are kept constant. Typically about ten sets of

recursions were required for a small wavelength configuration, diminishing to six at longer wavelengths.

The last important detail concerns the mixing of the old and new shifts during a self-consistency loop, required to obtain a stable convergence. As is well known in other types of calculations, charge self-consistency is very unstable. It was found that only approximately 4% of the output shift was required to be added to the input for stability to be achieved. With larger mixings, the charge self-consistency diverged rapidly.

5. The spectrum of longitudinal fluctuations

The original motivation for the calculations in this section comes from the accuracy of the estimated Curie temperature of Fe (McMullan, private communication) obtained using the approach of Lonzarich and Taillefer (1985). In this approach the finite temperature magnetic equation of state is assumed to be given by

$$B = A(T)M + bM^3 \tag{5.1}$$

where

$$A(T) = a + 2b\langle m_{\perp}^2 \rangle + 3b\langle m_{\parallel}^2 \rangle \tag{5.2}$$

in which a and b are the zero temperature Landau parameters discussed earlier, while $\langle m_{\perp}^2 \rangle$ and $\langle m_{\parallel}^2 \rangle$ represent the expectations of the transverse and longitudinal thermal magnetization fluctuations, respectively. The fluctuation dissipation theorem in the form,

$$\langle m_{\nu}^2 \rangle = \frac{4\hbar}{v} \sum_{\mathbf{q}} \int_0^{\infty} \frac{d\omega}{2\pi} n(\omega) \text{Im} \chi_{\nu}(\mathbf{q}, \omega) \tag{5.3}$$

where v is a normalization volume, $n(\omega)$ is the Bose function and $\nu = \parallel$ or \perp , is used to relate the expectations of the magnetization fluctuations to the dynamical susceptibility, $\chi_{\nu}(\mathbf{q}, \omega)$, which is assumed to have the form

$$\chi_{\nu}^{-1}(\mathbf{q}, \omega) = \chi_{\nu}^{-1} + c_{\nu}q^2 + \frac{i\omega}{\gamma_{\nu}q} + \dots \tag{5.4}$$

The Curie temperature, T_c , is now found from the condition that $\chi^{-1} = 0 = A(T_c)$. Assuming both that the system is isotropic and the upper q cutoff can effectively be taken to infinity, the integral in equation (5.3) can be carried out analytically to give

$$T_c = 2.387cM_0^{3/2}(\hbar\gamma)^{1/4}/k_B \tag{5.5}$$

where M_0 is the zero temperature moment given by $\sqrt{-a/b}$. In weakly ferromagnetic materials, such as MnSi and Ni₃Al, where estimates of parameters c and γ are available, this formula is found to give a remarkably good description of the observed T_c (Lonzarich and Taillefer 1985). Moreover, the predicted Curie temperatures of Fe and Ni obtained using equation (5.5) and estimates of c and γ turn out to

be in good agreement with experiment i.e., 900–1100 K and 560–680 K as compared with the experimental values of 1043 K and 627 K, respectively (McMullan 1989).

The parameters c_ν and γ_ν , as introduced in equation (5.4), describe the spectral distribution of the magnetic fluctuations. In weakly magnetic, cubic metals it is reasonable to assume that these are isotropic. However, this is not obviously the case in strong ferromagnets, such as Fe, and the calculations in this section were carried out in part to test this.

The total energies of the longitudinal fluctuations described below were calculated both from the fits to the fields and moments as described in section 3 and by direct evaluation of the total energy using the new quadrature procedure described in section 4. Since one requires a number of runs with different sets of $\{m_j\}$ to evaluate the Landau energy, one can run the two methods at the same time. The final answers were found to be exactly the same. Lastly, all configurations were taken in the [001] direction.

Figure 2 shows the total energy of longitudinal fluctuations for the Brillouin zone case ($q = \pi$) in the three charge transfer approximations discussed to above. Explicitly this configuration consists of two sites, with magnetization $m_{\text{FM}} + \delta m$ and $m_{\text{FM}} - \delta m$. As expected the total energy depends linearly on $(\delta m)^2$. Indeed the accuracy with which this expectation is confirmed is almost surprising.

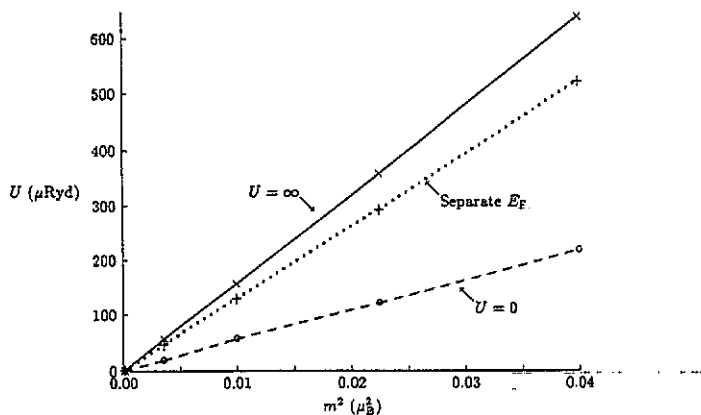


Figure 2. Energy of longitudinal fluctuations at the Brillouin zone against amplitude squared of the magnetization wave. The expected linearity of the behaviour is evident, even surprising in its accuracy.

The behaviour of the energies for the different approximations for treating charge transfer also confirms our expectations. There is a marked difference between the $U = \infty$ and the $U = 0$ approximations with the 'local Fermi energy' approximation being a good approximation to the $U = \infty$ result showing that local charge neutrality is the most important contribution.

There is one final detail which deserves mentioning. In working out the energy of an excitation of a given q and fixed amplitude one is effectively assuming an average over configurations with that amplitude and all possible phases. Though in the continuum limit these are obviously all the same, this is clearly not so when one has discrete sites. The configurations we choose are all symmetric in the distribution of sites above and below the ferromagnetic moment i.e., there is always one site at the maximum of the wave, one at the minimum and two at the ferromagnetic value.

In this way we are always comparing configurations of the same phase. The only value of q for which we cannot do this is at the Brillouin zone. Here we average between the configuration with phase zero (the values of figure 2) and that of the one with phase π i.e., the ferromagnetic energy.

This point is important when comparing energies of configurations of different wavelength as shown in figure 3. These are the results for a fixed amplitude of $0.1 \mu_B$. This represents a 4.5% deviation from the ferromagnetic state and yields energy changes larger than the numerical error involved but small enough that the nonlinear dependencies of the quantities does not dominate.

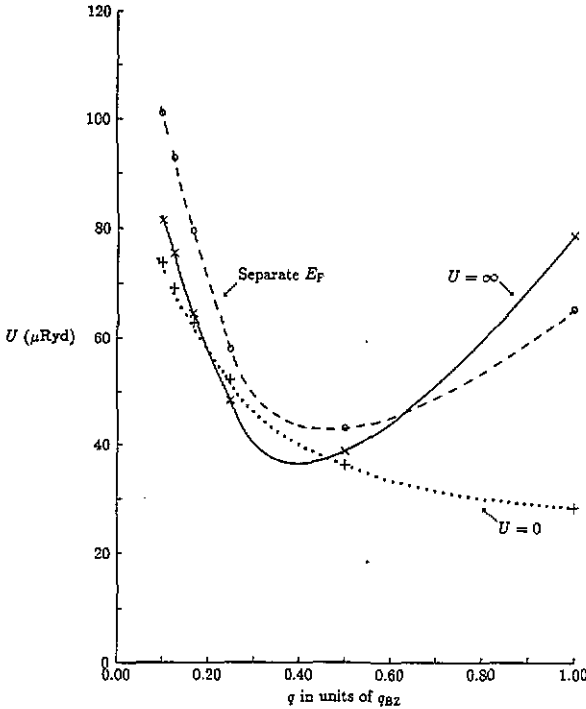


Figure 3. Spectrum of longitudinal fluctuations of amplitude $0.1 \mu_B$. The energy is taken relative to the ferromagnetic ground state. The result for the Brillouin zone configuration is adjusted for phase averaging as described in the text.

Surprisingly the total energy for a configuration of non-zero q turns out to be substantially smaller than the $q \rightarrow 0$ limit, before increasing again at the Brillouin zone. As expected the $U = 0$ approximation underestimates the energy of the configuration for the full range of q . There is only one point ($q = \pi/4$) where this is not true. It is probable though, that a better approximation for the average over the phases would yield better agreement since it greatly influences the result at $q = \pi/2$. The small q limit shows that all curves are proportional to q^2 as we would expect. Hence even though the negative gradient is surprising there is no reason to suspect that the results are unphysical.

These curves can be interpreted according to the following picture. If we assume that the interactions are completely local, the total energy for a fixed amplitude, would be constant as a function of q . We know that this is a very bad approximation but it should be reasonable in the $q \rightarrow 0$ limit. Moreover one could argue that it

should also apply better at the Brillouin zone since the distortions are such that the local term dominates especially if there is a strong next-nearest neighbour coupling. In this case it is not surprising that the Brillouin zone energy and the $q \rightarrow 0$ limit are quite similar. In between the non-local coupling drives the energy down which is strange but not unreasonable.

This result has one possible implication for the long standing problem of short range order in Fe above T_c (see Capellmann 1986 for a recent review). If the system favours short range order then this could well show up in the longitudinal as well as the transverse energies. One can think of this as a Fermi surface effect. If there are fairly flat regions connected by a given q then this would show up both in the longitudinal susceptibility and in the transverse. So the definite minimum around $\lambda = 4$ is interesting in this context. If the same length scale were to apply to transverse excitations this would imply a nearest neighbour angle around 45° .

Acknowledgments

We acknowledge with pleasure many conversations with J H Samson and C M M Nex. We are also indebted to D G Pettifor for illuminating discussions on charge self-consistency. We thank the SERC for the granting of CRAY time. One of us (MUL) thanks the Fondazione *Angelo della Riccia*, Florence for financial support.

References

- Capellmann H 1986 *Metallic Magnetism* ed H Capellmann (Berlin: Springer)
- Cooke J F, Lynn J W and Davis H L 1980 *Phys. Rev. B* **21** 4118
- Fritsche L, Noffke J and Eckardt H 1987 *J. Phys. F: Met. Phys.* **17** 943
- Haydock R 1980 *Solid State Physics* **35** 215
- Hubbard J 1979 *Phys. Rev. B* **20** 4584
- Lonzarich G G and Taillefer L 1985 *J. Phys. C: Solid State Phys.* **18** 4399
- Luchini M U and Heine V 1989 *J. Phys.: Condens. Matter* **1** 8961
- Luchini M U and Nex C M M 1990 *J. Phys.: Condens. Matter* **2** 3497
- McMullan G J 1989 *PhD Thesis* University of Cambridge (unpublished)
- Muniz R B, Cooke J F and Edwards D M 1985 *J. Phys. F: Met. Phys.* **15** 2357
- Nex C M M 1978 *J. Phys. A: Math. Gen.* **11** 653
- 1984 *Comput. Phys. Comm.* **34** 101
- Schwarz K and Mohn P 1984 *J. Phys. F: Met. Phys.* **14** L129
- Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
- Small L M and Heine V 1984 *J. Phys. F: Met. Phys.* **14** 3041
- Stollhoff G, Otés A M and Heine V 1990 *Phys. Rev. B* **41** 7020
- Sutton A P, Finnis M W, Pettifor D G and Ohta Y 1988 *J. Phys. C: Solid State Phys.* **21** 35
- Van Camp P E, Van Doren V E and Devreese J T 1983 *Ab Initio Calculation of Phonon Spectra* ed J T Devreese, V E Van Doren and P E Van Camp (New York: Plenum)
- Wakoh S, Edwards D M and Wohlfarth E P 1971 *J. Physique Coll.* **32** C1 1073
- Wang C S, Prange R E and Korenman V 1982 *Phys. Rev. B* **25** 5766
- Wood J H 1962 *Phys. Rev.* **126** 517
- You M V and Heine V 1982 *J. Phys. F: Met. Phys.* **12** 177