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Axial pressures of non-collinear magnets in γ-Mn and γ-Fe

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Abstract. A modified expression for the axial pressure is derived and implemented within an LMTO-ASA framework. The axial pressures of non-collinear antiferromagnets in FCC manganese and iron are calculated and used to make predictions on the axial distortion and relative stability of the phases.

1. Introduction

The FCC alloys of Mn and Fe exhibit a number of phase transitions as a function of alloy concentration (e.g. Honda *et al* 1976). These changes involve both the structural parameters and the magnetic order, and while the magnetic phases are known to be type I antiferromagnets their exact structures have not been determined conclusively. It is believed (Uchishiba 1971, Endoh and Ishikawa 1971, Tsunoda *et al* 1987, Long *et al* 1987) that some of these phases may exhibit non-collinear magnetism, there being no unique axis for spin quantization. It was shown in a previous paper (Crockford *et al* 1991, hereafter referred to as I) how these non-collinear structures may be handled in an LMTO-ASA calculation (Andersen 1975) and attention was focused on three representatives, the single, double and triple spin density waves, referred to as the SSDW, DSDW and TSDW respectively. The arrangements of spins for these cases are shown in figure 1, which depicts an octant of the cubic unit cell. The SSDW is the simple collinear antiferromagnet characterized by a single wavevector $\boldsymbol{Q}$, whereas the DSDW and TSDW are true non-collinear magnets, characterized by two and three $\boldsymbol{Q}$ vectors respectively.

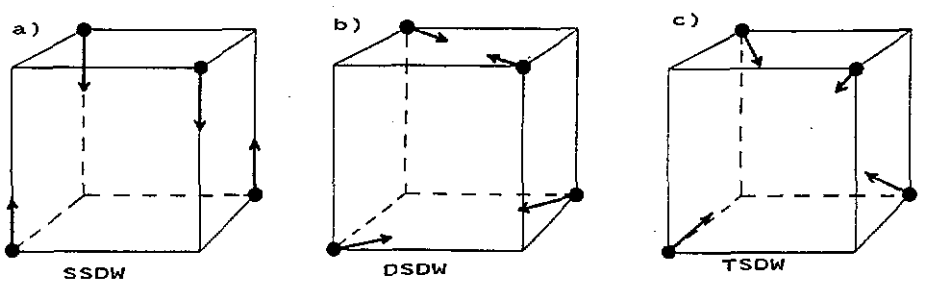

Figure 1. Spin arrangements in an octant of the FCC lattice for the (*a*) SSDW, (*b*) DSDW and (*c*) TSDW antiferromagnets.

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It is clear from figure 1 that while the magnetic structure of the TSDW retains cubic symmetry, those of the SSDW and DSDW do not, and therefore allow for a magnetically driven tetragonal distortion. Experimentally, the SDW phases of Mn and Fe alloys appear to distort in a manner consistent with a *localized* spin picture. In the SSDW a tetragonal distortion to $c/a < 1$ is observed (Smith and Vance 1969). The result of such a distortion is clearly to make the parallel spins of the ferromagnetic planes further apart and adjacent planes, of opposite spin, closer together (see figure 1). Conversely, in the DSDW the lattice distorts with $c/a > 1$ (Uchishiba 1971). The phases which remain cubic can similarly be identified with the TSDW structure (Endoh and Ishikawa 1971). In this paper the self-consistent potentials obtained in I will be used as input for the calculation of axial pressures, i.e. the tendency for the cubic lattice to favour a tetragonal distortion (Cade 1981). The results will be used to investigate the effects of the magnetic order on the crystal structure.

The most straightforward way to determine the lattice constant a of a material using LMTO-ASA is to plot the total energy for a number of different values of a and look for a minimum. However, the total energy difference due to a small change in a is very small compared to the energies themselves. To avoid having to obtain total energies accurate to many decimal places it is usual to work with the pressure rather than the total energy. The bulk or isotropic pressure (Liberman 1971) can be obtained from the derivative of the Kohn–Sham energy (Kohn and Sham 1965) with respect to the lattice constant and corresponds to the outward pressure exerted on the boundaries of the unit cell. Similarly we can define an axial pressure using the derivative of the Kohn–Sham energy with respect to c/a (Cade 1981). Evaluated at constant volume, this corresponds to a pressure on the unit cell boundaries that acts so as to change only the c/a ratio. The equilibrium value of a or c/a is determined by finding the value for which the respective pressure is zero. In practice this procedure works well for the lattice constant a (Pettifor 1977, Andersen *et al* 1985) but does not work in general for the c/a ratio (Crockford 1990). One reason for this failure lies in the approximate treatment given to electrostatic forces in the ASA. The importance of these forces for non-isotropic distortions has been demonstrated by Christensen (1984). As far as the axial pressure is concerned the approximation of the ASA lies in the replacement of the Wigner–Seitz cells by neutral Wigner–Seitz spheres. In the case of a magnetically driven tetragonal distortion we can avoid these problems by working only with the reference cubic structures shown in figure 1, for which there is no charge contribution to the axial pressure. Any axial pressure we find in the SSDW or DSDW phases can then be attributed entirely to the magnetism. Although no attempt is therefore made to find the equilibrium c/a ratio by performing calculations on non-cubic structures, this can be estimated from the axial pressure in the 'ideal' structure.

The first self-consistent LMTO-ASA calculation for a SSDW structure was performed by Cade (1980) on Mn. Cade went on to perform an ASA axial pressure calculation for the SSDW and obtained the *correct direction* for the distortion (Cade 1981) despite the approximation implicit in the ASA. In this paper we calculate the value for the SSDW in both Mn and Fe using a modified expression for the axial pressure, and we also calculate values for the non-collinear DSDW and TSDW. Substituting these into a simple elasticity model we obtain estimates of the equilibrium distortion and predict the relative stabilities of the phases of Mn.

2. A first-order expression for the axial pressure

In this section we evaluate the axial pressure in the ASA and arrive at an expression which is similar to Cade's (1981) result, but involves a different sd contribution and is correct to a higher order in the non-spherical component of the charge density.

The basic definition of the axial pressure that we adopt is due to Cade (1981):

$$P = -\frac{1}{6V}\frac{\mathrm{d}E}{\mathrm{d}\lambda} \tag{1}$$

where V is the volume of the unit cell, E is its Kohn–Sham energy and λ is the distortion parameter. The derivative of the Kohn–Sham energy with respect to a given strain is readily obtained (Crockford 1990) from a scaling-type calculation (Fock 1930), provided the lattice can be divided into regions that are electrically neutral. In the ASA we assume that these regions are spherical. The derivative can be re-expressed as a surface integral (Liberman 1971) using the sort of argument presented by Slater (1933) in his proof of the virial theorem, and substituting into (1) from which we obtain

$$P = \frac{1}{16\pi s^3}\sum_i \int \mathrm{d}^2\boldsymbol{S}\cdot[(\nabla\psi_i^*)\boldsymbol{r}\cdot\boldsymbol{\varepsilon}\cdot\nabla\psi_i - \psi_i^*\nabla(\boldsymbol{r}\cdot\boldsymbol{\varepsilon}\cdot\nabla\psi_i) + \mathrm{cc}]$$
$$+ \frac{1}{8\pi s^3}\int \mathrm{d}^2\boldsymbol{S}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{r}n^2(\boldsymbol{r})\frac{\mathrm{d}\varepsilon_{\mathrm{xc}}}{\mathrm{d}n} \tag{2}$$

where the i-summation is over the occupied valence bands, ψ_i is the wavefunction for band i, $n(\boldsymbol{r})$ is the charge density and s is the sphere radius. In (2) and in what follows the summations over spin and site are implicit. The $\boldsymbol{\varepsilon}$ in (2) is the strain tensor and for a volume-conserving axial distortion, can be written as

$$\boldsymbol{\varepsilon} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \tag{3}$$

The normalization of $\boldsymbol{\varepsilon}$ is chosen for consistency with (1).

To determine P we now have two integrals to evaluate. The first can be approached by directly inserting the expansion for ψ_i in terms of LMTO basis states, and using the Schrödinger equation to eliminate second derivatives. We define a generalized density of states

$$n_{\alpha\beta}(E) = \frac{1}{8\pi}\sum_i \int_{\mathrm{BZ}} \mathrm{d}\boldsymbol{k}\, A_{i\alpha\beta}\,\delta(E - E_{i\boldsymbol{k}}) \tag{4}$$

where (for a given i)

$$A_{\mathrm{pp}} = \tfrac{1}{5}\left(2|u_{\boldsymbol{k}10}|^2 - |u_{\boldsymbol{k}11}|^2 - |u_{\boldsymbol{k}1-1}|^2\right) \tag{5}$$
$$A_{\mathrm{dd}} = \tfrac{1}{7}\left(2|u_{\boldsymbol{k}20}|^2 + |u_{\boldsymbol{k}21}|^2 + |u_{\boldsymbol{k}2-1}|^2 - 2|u_{\boldsymbol{k}22}|^2 - 2|u_{\boldsymbol{k}2-2}|^2\right) \tag{6}$$
$$A_{\mathrm{sd}} = \frac{1}{\sqrt{5}}(u_{\boldsymbol{k}00}^* u_{\boldsymbol{k}20} + u_{\boldsymbol{k}20}^* u_{\boldsymbol{k}00}) \tag{7}$$

and u_{klm} is the eigenvector corresponding to E_{ik}. These quantities correspond to the 'axial weights' given by Cade (1981) and are the only combinations which are consistent with the tetragonal distortion of (3). They would be zero for a spherically symmetric charge density. The first integral in (2) can now be written as

$$\frac{1}{4\pi s^3}\int_{-\infty}^{E_F} s\,dE\left\{n_{pp}\phi_1^2\left[D_1^2+D_1-2+s^2(E-v_{eff})\right]\right.$$
$$+n_{dd}\phi_2^2\left[D_2^2+D_2-6+s^2(E-v_{eff})\right]$$
$$\left.+n_{sd}\phi_0\phi_2\left[-D_0D_2+D_2-2D_0+3-s^2(E-v_{eff})\right]\right\} \tag{8}$$

where D_j is the logarithmic derivative of the LMTO basis function χ_j at the sphere (Andersen 1975). This expression disagrees with Cade (1981), who gives the coefficient of n_{sd} as $\phi_0\phi_2(D_0-D_2)$.

The second integral in (2) involves the exchange correlation ε_{xc}, which is a *non-linear* function of $n(r)$. In the spirit of the ASA we assume that the non-spherical component δn of n is small, and expand n to first order about the spherical average n^{ASA}

$$n = n^{ASA}+\delta n+O(\delta n)^2\,. \tag{9}$$

Differentiating $n^2\,d\varepsilon_{xc}/dn$ with respect to n and using the definition (Kohn and Sham 1965) of v_{xc} we obtain

$$v_{xc}-\varepsilon_{xc}+n\left(\frac{dv_{xc}}{dn}-\frac{d\varepsilon_{xc}}{dn}\right)=n\frac{dv_{xc}}{dn}\,. \tag{10}$$

Following the same procedure as with the first integral leads to a final expression (more details of the derivation may be found in Crockford (1990))

$$P=\frac{1}{4\pi s^3}\int_{-\infty}^{E_F} s\,dE\left[n_{pp}\phi_1^2(D_1^2+D_1-2+\Delta)+n_{dd}\phi_2^2(D_2^2+D_2-6+\Delta)\right.$$
$$\left.+n_{sd}\phi_0\phi_2(-D_0D_2+D_2-2D_0+3-\Delta)\right] \tag{11}$$

where Δ is given by,

$$\Delta=s^2\left(E-v_{eff}(s)+n^{ASA}(s)\left.\frac{dv_{xc}}{dn}\right|_{n^{ASA}(s)}\right)\,. \tag{12}$$

Cade's (1981) result is similar to this but uses ε_{xc} instead of v_{xc} in (12), indicating that it is correct only to zeroth order in δn.

3. Implementation

The axial pressures for the SSDW, DSDW and TSDW in Mn and Fe were calculated from the self-consistent potentials obtained in I. To do this the LMTO program was modified to calculate the axial weights (5)–(7) rather than spherical weights (Skriver 1984), and the code to evaluate (11) was inserted after the charge density routine (the

charge density being needed to calculate v_{xc}). It should be noted that the calculation of the axial weights does not interfere with the representation of the SDW: the former involves manipulation of the eigenvectors using lm labels only while the latter involves only the spin/sublattice labels (see I). As previously the k-space integration was performed over the orthorhombic wedge of the Brillouin zone with a mesh of 64 points.

The generalized densities of states (4) being available, evaluation of (11) can be done using a moment expansion (Skriver 1984). Recognizing that each term in (11) is of the form

$$\int_{-\infty}^{E_F} \mathrm{d}E\, n_{ll'}(E)\, f_{ll'}(E,s) \tag{13}$$

where $f_{ll'}(E,s) \equiv f(\phi_l, \phi_{l'}, \dot{\phi}_l, \dot{\phi}_{l'})$, we can expand $f_{ll'}$ as a Taylor series about $E = E_\nu$ to obtain

$$g_0 \int_{-\infty}^{E_F} \mathrm{d}E\, n_{ll'}(E) + g_1 \int_{-\infty}^{E_F} \mathrm{d}E\, n_{ll'}(E)\,(E - E_\nu) + \tfrac{1}{2} g_2 \int_{-\infty}^{E_F} \mathrm{d}E\, n_{ll'}(E)\,(E - E_\nu)^2 + \cdots . \tag{14}$$

Here the coefficient g_n is the nth derivative of $f_{ll'}$ with respect to E and is a function of ϕ_l and $\phi_{l'}$, and their energy derivatives, evaluated at (E_ν, s). By terminating the expansion at third order it is possible to evaluate the g_ns in terms of the standard LMTO potential parameters (Andersen 1975). In all cases treated the expansion was very well converged when taken to this order.

3. Results and discussion

The results for the axial pressures are given in table 1. The values for Mn are clearly in accord with the predictions of the localized electron picture: the SSDW tends to shrink along the c axis, the DSDW to expand, and the TSDW remains cubic. Indeed, the fact that the magnetic space group of the TSDW is cubic implies that the pressure for the TSDW is identically zero, as there can be no driving force for an axial distortion (this also follows from the form of the axial weights—see Cade (1981)). The small value we find arises from the imperfect Brillouin zone integration. Using the value for the TSDW in Mn as a yardstick we should probably take the pressure for the SSDW in Fe to be also zero. Hence, the only non-zero pressure among the Fe materials belongs to the DSDW, and its sign is not consistent with the localized picture. However, even here the value is an order of magnitude less than the corresponding pressure in Mn. By the same argument used for the TSDW the pressures for paramagnetic Mn and Fe are also forced to be zero. The non-zero values obtained are therefore *purely magnetic* in origin.

Table 1. Axial pressures for SDW materials (kbar).

	SSDW	DSDW	TSDW
Mn	−11.596	4.488	0.049
Fe	−0.078	−0.248	0.001

The axial pressures can be used in a classical elasticity model (see appendix) to estimate the deviation of the c/a ratio from the cubic value at equilibrium (table 2), and the energy saving associated with it. To do this we require experimental values for the elastic constants of FCC Mn and Fe, but these have not been measured because the γ phases are not sufficiently stable. We therefore resort to using the elastic constants for neighbouring Ni, for which $C' = (C_{11} - C_{12})/2 = 470$ kbar (Smithell 1983). Although the values for the deviation in table 2 are therefore no more than rough estimates, the results for the SSDW and DSDW in Mn are in fair agreement with the respective experimental estimates of −6% (Cowlam *et al* 1977, Smith and Vance 1969) and 1.5% (for Mn with 18.5% Ni: Honda *et al* 1976) while for Fe a distortion from the cubic structure does not appear to have been reported. Adding the energy savings to the ASA total energies for the Mn phases at ideal c/a (Crockford *et al* 1991) we obtain the equilibrium total energies of table 3. From these we deduce that the most stable phase for pure FCC Mn would be SSDW, in agreement with experimental data (Endoh and Ishikawa 1971).

Table 2. Estimated % deviation form $c/a = 1$.

	SSDW	DSDW	TSDW
Mn	−3.8	1.4	0.02
Fe	−0.02	−0.08	0.0003

Table 3. Estimated equilibrium total energy for Mn systems.

	SSDW	DSDW	TSDW
Total energy (Ryd)	−126.127	−126.126	−126.125

4. Conclusion

The main point to emerge from this work is that when applied to *magnetic* systems the ASA axial pressure gives very reasonable results. Given that the axial pressures exhibited in the materials treated are a consequence of the magnetic order only it is perhaps not surprising that the essentially *charge-dependent* inaccuracies of the ASA should not be relevant. We find a considerable tendency for the SSDW and DSDW structures in FCC Mn to distort, while the axial pressure in FCC Fe is essentially zero. It is also interesting to note that our results for Mn, which are obtained within the itinerant electron framework provided by spin-density functional theory (von Barth and Hedin 1972), give tetragonal distortions which are consistent with a picture of localized spins attempting to bring favourably aligned neighbours closer and push unfavourable neighbours apart.

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Appendix

Consider the second-order expansion of the classical elastic energy about equilibrium (Kittel 1968)

$$\frac{E}{V} = \tfrac{1}{2}\sum_{i=1}^{6}\sum_{j=1}^{6} C_{ij}e_i e_j \tag{A1}$$

where the C_{ij}s are the elastic constants and the e_is are the strain components. For a volume-conserving axial strain we have $e_1 = e_2 = -\lambda$ and $e_3 = 2\lambda$, so (A1) becomes

$$\frac{E}{V} = 6\lambda^2 C' \qquad \text{where} \quad C' = \tfrac{1}{2}(C_{11} - C_{12}). \tag{A2}$$

Differentiating (A2) with respect to λ and substituting from (1) gives

$$\lambda = -\frac{1}{2}\frac{P}{C'}. \tag{A3}$$

Putting

$$c' = c(1 + 2\lambda) \tag{A4}$$

and

$$a' = a(1 - \lambda) \tag{A5}$$

we can derive an expression for λ in terms of c/a, namely

$$\lambda = \frac{1 - (c/a)_{\text{eqm}}}{3(c/a)_{\text{eqm}}} + \mathrm{O}(\lambda^2). \tag{A6}$$

Given the axial pressure P for $c/a = 1$ we can use (A3) and (A6) to estimate the deviation from $c/a = 1$ at equilibrium, and (A2) and (A3) to obtain the corresponding energy saving.

References

Andersen O K 1975 *Phys. Rev.* B **12** 3060

Andersen O K, Jepsen O and Glötzel D 1985 *Highlights of Condensed Matter Theory* ed F Bassani *et al* (Amsterdam: North-Holland) p 59

Cade N A 1980 *J. Phys. F: Met. Phys.* **10** L187

Cade N A 1981 *J. Phys. F: Met. Phys.* **11** 2399

Christensen N E 1984 *Solid State Commun.* **49** 701

Cowlam N, Bacon G E and Gillott L 1977 *J. Phys. F: Met. Phys.* **7** L315

Crockford D J 1990 *PhD Thesis* University of Bath

Crockford D J, Bird D M and Long M W 1991 *J. Phys.: Condens. Matter* **3** 8665

Endoh Y and Ishikawa Y 1971 *J. Phys. Soc. Japan* **30** 1614

Fock V 1930 *Z. Phys.* **63** 855

Honda N, Tanji Y and Nakagawa Y 1976 *J. Phys. Soc. Japan* **41** 1931

Kittel C 1968 *Introduction to Solid State Physics* 3rd edn (New York: Wiley)

Kohn W and Sham L J 1965 *Phys. Rev.* **140** 1133

Liberman D A 1971 *Phys. Rev.* B **3** 2081
Long M W, Lowde R D and Sakata M 1987 *Rutherford Appleton Report* RAL-88-022
Pettifor D G 1977 *CALPHAD* vol 1 (Oxford: Pergamon) p 305
Skriver H L 1984 *The LMTO Method* (Berlin: Springer)
Slater J C 1933 *J. Chem. Phys.* **1** 687
Smith J H and Vance E R 1969 *J. Phys. C: Solid State Phys.* **2** 761
Smithell C J 1983 *Smithell's Metals Reference Book* (London: Butterworths)
Tsunoda Y, Kunitomi N and Nicklow R M 1987 *J. Phys. F: Met. Phys.* **17** 2447
Uchishiba H 1971 *J. Phys. Soc. Japan* **31** 436
von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629