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Magnetic Susceptibility of V, Cr, Mn and Mo and Magnetism in Cr and Mn

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Abstract

A tight-binding formulation has been used to compute the many-body enhanced magnetic susceptibility $\chi(q)$ of transition metals around Cr in the periodic table. The pole structure of $\chi(q)$ indicates paramagnetism for V and Mo, antiferromagnetism for Cr and γMn, and ferromagnetism for δMn at $T = 0$ K.

1. Introduction

An extensive literature exists on incommensurate antiferromagnetism in transition metals and alloys (Steinitz 1986; Arrott 1966; Fawcett 1988; Grier *et al.* 1985; Overhauser 1962; Lomer 1962, 1964). Theoretical interpretations are frequently based upon the wave-vector dependent magnetic susceptibility $\chi(q)$ and the paramagnetic state, but parameter-free quantitative calculation of $\chi(q)$ including many body enhancements have not been available.

The purpose of this paper is to report the first quantitative calculation of the wave-vector dependence of the many-body enhanced magnetic susceptibility of a group of transition metals at $T = 0$ K based upon accurate band structure calculations. The susceptibility $\chi(q)$ has been computed along the cubic axis and confirmation of the original ideas of Overhauser (1962) obtained. The key quantities computed were the random phase approximation (RPA) to the susceptibility $\chi(q)$ and the enhanced susceptibility $\chi(q)$. For a real solid these require calculation of complicated matrix elements and band structures at many points in the Brillouin zone, three-dimensional principal value integration, and summation over many bands. Evaluation of $\chi(q)$ requires computation and inversion of additional large matrices. Development of fast, accurate methods of generating band structures throughout the Brillouin zone, accurate numerical integration methods and a tractable expression for the many-body enhancements for $\chi(q)$ have now made the calculation feasible (Slater and Koster 1954; Papaconstantopoulos 1986; Rath and Freeman 1975; Callaway *et al.* 1983).

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2. Theory

According to the theory of Callaway *et al.* (1983), the many-body-enhanced susceptibility tensor may be written in the form

$$\chi(\boldsymbol{q}, \omega) = \sum_{ij,lm} I_{ij}(\boldsymbol{q}_s)\, \Gamma_{ij,lm}\, I_{lm}(-\boldsymbol{q}_t)\,, \tag{1}$$

where $\Gamma_{ij,lm}$ is the enhanced wave-vector and frequency-dependent susceptibility on an orbital basis and $I_{ij}(\boldsymbol{q})$ is an atomic form factor. The enhanced susceptibility on the orbital basis is given in terms of the RPA susceptibility on an orbital basis $\gamma_{ij,lm}$ by

$$\Gamma_{ij,i'j'} = \sum_{l,m} \gamma_{ij,lm}[(I - X)^{-1}]_{lm,i'j'}\,, \tag{2}$$

with

$$X_{ij,i'j'} = \sum_{st,lm} I_{ij}(-\boldsymbol{P}_s)\, \Lambda(\boldsymbol{K}_s - \boldsymbol{K}_t)\, I_{lm}(P_t)\, \gamma_{lm,i'j'}\,. \tag{3}$$

Here Λ is a matrix in reciprocal-lattice vectors, $\boldsymbol{K}_s$ and $\boldsymbol{K}_t$, which is related to the exchange-correlation potential used in the band structure calculation. The matrices Λ, γ and I are defined in the paper by Callaway *et al.* (1983). In obtaining equation (1) it was necessary to assume that orbitals contributing to the enhancement do not overlap on adjacent sites. With this assumption the very large reciprocal lattice basis for χ_{st} necessary in a transition metal has been exchanged for a smaller orbital basis. This step is essential because of the matrix inversion required in equation (2). The poles of $\chi_{st}(q,\omega)$ define the spin-wave dispersion relation and can be found from the equation

$$\mathrm{Re}[D(q, \omega)] = 0\,, \tag{4}$$

where $D(q,\omega) = \det[I-X]$. For the spin-density-wave ground state the condition simplifies to $D(q,0) = 0$.

Even with the approximation made, evaluation of equation (1) is a formidable task. To accelerate calculation of γ, orthogonal two-centred Slater–Koster (SK) (1954) fits were used for the band structures: Papaconstantopoulos (1986) for V, Mn and Mo and Pattnaik *et al.* (1983) and Laurent *et al.* (1981) for Cr. The method of Callaway *et al.* (1983) was used to obtain matrix elements, except new Clement-type wavefunctions were obtained by a variational calculation employing the self-consistent muffin-tin potentials of Moruzzi *et al.* (1978).

The integrals $I_{ij}(q)$ were computed from the resulting wavefunctions. The matrix Λ was computed with the same wavefunctions and Barth–Hedin (1972) potentials were constructed from the charge densities of Moruzzi *et al.* (1978). Angular integrals needed for Λ were done with a symbolic manipulator code and radial integrals evaluated numerically. The full matrix Λ was employed with no diagonal approximations on the orbital basis. The γ matrix was computed using 55 (506 for Cr and 505 for γMn) points in the irreducible part of the Brillouin zone and the analytic tetrahedron method (ATM; Rath and Freeman 1975).

Table 1. Uniform susceptibilities for V, Cr, Mn and Mo

The RPA susceptibility $\chi_0(0)$ is measured in units of μ_B^2/Ry, where μ_B is the Bohr magneton. Here R_1 and R_2 are the computed enhancement factors $\chi(0)/\chi_0(0)$ for the present work and the work of Janak (1977). The last two columns compare the magnitude of the radial exchange-correlation integral λ of this work with the exchange-correlation integral of Janak. Since λ is multiplied by a matrix which depends upon various angular integrals it cannot be compared directly with I. To emphasise the similar variation, λ has been normalised to give agreement for vanadium by multiplying by (0·026/0·509). For BCC Mn the same radial integral was assumed as for FCC Mn, as suggested by Janak (cf. the values for scandium)

Element	$\chi_0(0)$	R_1	R_2	λ (Ry)	I (Ry)
V	32·73	2·51	2·34	0·026	0·026
Cr	8·40	1·30	1·36	0·029	0·028
Mn(FCC)	28·24	11·99	2·74	0·033	0·030
Mn(BCC)	39·31	−1·44	—	0·033	0·030
Mo	7·05	1·18	1·23	0·025	0·022

Table 2. Enhanced susceptibilities for V, Cr, Mn and Mo along the (100) direction from Γ to H(X for FCC)

Units of χ are μ_B^2/Ry and a is the cubic lattice constant

$(a/2\pi)q$	V	Cr	Mn(FCC)	Mn(BCC)	Mo
0·000	82·3	11·0	479·1	−56·6	8·3
0·125	61·9	12·9	213·7	−53·0	9·3
0·250	43·1	17·5	160·1	−58·1	11·6
0·375	38·0	26·3	163·1	−74·4	14·9
0·490	38·7	36·1	179·2	−99·0	17·7
0·500	38·6	37·1	186·8	1533·6	17·9
0·625	35·5	51·5	1172·2	143·7	19·9
0·750	29·7	78·4	−743·9	137·3	21·6
0·875	24·4	163·8	−414·8	167·1	22·7
0·920	22·6	347·1	−477·0	165·2	23·4
0·930	22·3	493·9	−489·3	163·8	23·5
0·950	21·5	9500·0	−510·6	160·0	22·4
0·955	21·4	−833·4	−515·0	158·8	22·0
0·960	21·2	−420·6	−519·4	157·6	21·7
1·000	19·8	−14·5	−541·0	145·8	20·0

3. Results

The results of these calculations for $K_s = K_t = 0$ are summarised in Tables 1 and 2 and Figs 1 and 2. The uniform susceptibilities $\chi(q = 0)$ are compared with the results of Janak (1977) in Table 1. In the present work only χ_{dd} was enhanced, since s and p parts of the conduction bands were free-electron like and could not satisfy approximations leading to equation (1). Even though s and p contributions represent less than 10% of the contribution to χ, they were included in the unenhanced susceptibility χ_0, using a constant matrix element approximation in order to give the correct $q = 0$ limit to χ_0. Considering the fact that only χ_{dd} was enhanced, and different band structures and wavefunctions were used, agreement with variational estimates of Janak is better than expected. Enhancing the other terms would increase $\chi(0)/\chi_0(0)$ above the variational minimum values of Janak.

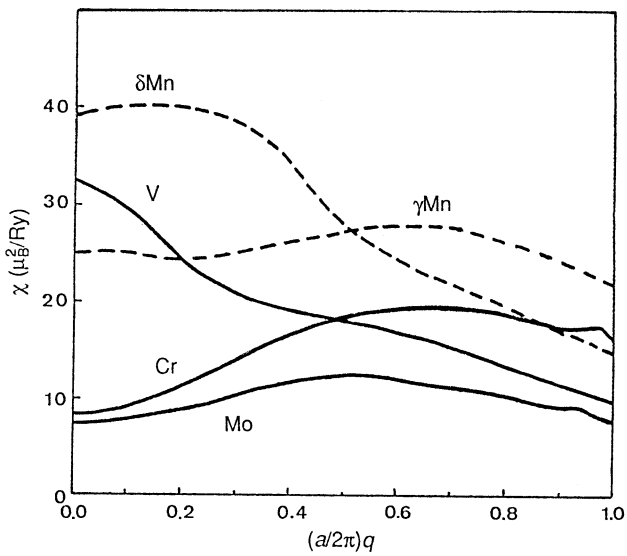

Fig. 1. RPA susceptibility for V, Cr, Mn and Mo along a cubic axis.

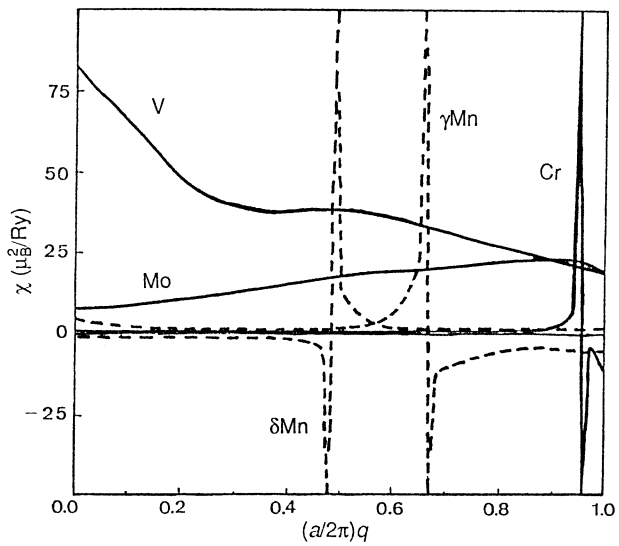

Fig. 2. Exchange-correlation enhanced susceptibility for V, Cr, Mn and Mo along a cubic axis. For Cr and Mn, χ has been divided by 100 to plot on the same scale.

The largest difference, for FCC Mn, may be attributed to the quality of the two-centred orthogonal SK fit for the band structure, which included only first and second neighbours, and to rapid changes in the density of states at the Fermi energy $D(E_F)$ for small changes in E_F. Included in Table 1, for the portion of the periodic table of interest here, are the computed exchange-correlation radial integrals for the d orbitals, defined in equation (4·7) of Callaway *et al.* (1983),

through the relation $\theta_{iji'j'} = \lambda\theta^{a}_{iji'j'}$, where 'a' indicates the angular part of the integral. This quantity, while defined differently, is analogous to the exchange correlation integral of Janak (1977), except that here a matrix is involved. The variation between elements is the same for both quantities.

The wave-vector-dependent RPA susceptibility is shown in Fig. 1. The results for Cr are similar to those reported by Gupta and Sinha (1971), except that the broad peak is higher here. Effects of Fermi surface nesting are clear from the peak in Cr at 0·96. The peak is greatly reduced in Mo because of matrix element effects involving the 4d wavefunction. Increasing the number of numerical integration points sharpens the peak, but even in Cr with the best SK fit it was not possible to obtain an absolute maximum at the sharp peak. Previous experience with logarithmic functions and the ATM suggests that this could be a numerical problem with sampling or with insufficient accuracy in the band structure itself (see Fig. 3 of Fry *et al.* 1977). Whether there is a singularity in $\chi_0(q)$ in Cr cannot be resolved, but it is unlikely in Mo. Changes in Fermi surface nesting with the Fermi energy have been used successfully to explain the concentration dependence of the wave vector of the spin-density waves in Cr(V, Mn) alloys (Zhao *et al.* 1986)—Fig. 1 offers a plausible explanation for antiferromagnetism in the portion of the periodic table considered here. Even though Mo has a Fermi surface almost identical to Cr it is not predicted to be antiferromagnetic; V is paramagnetic; BCC and FCC Mn could possibly be antiferromagnetic. Inclusion of enhancement to $\chi_0(q)$ removes uncertainty about these statements and changes them.

Fig. 2 and Table 2 show the enhanced results, $\chi(q)$. Note that enhancement is so strong in Cr and Mn that the susceptibility is plotted on a different scale and that Cr has a pole at $q = 0{\cdot}95$, in agreement with experiment. The q dependence of the enhancement is very strong for Cr and Mn, but weak for V and Mo: even though χ/χ_0 and $D(E_F)$ are smaller for Cr than V, enhancement effects are dramatically different. Equation (4) is satisfied only for Cr and Mn.

The case of Mn is especially interesting since it falls between antiferromagnetic chromium and ferromagnetic iron. Experimentally it is found to have four allotropic phases, α, β, γ and δ. The high temperature phases, γ and δ, are FCC and BCC respectively, but the room temperature phase α is BCC with 29 atoms per unit cell and becomes magnetic at low temperatures (Arrott 1966). The present itinerant theory is based upon a $T = 0$ K calculation, but clearly predicts incommensurate antiferromagnetic behaviour for FCC Mn and ferromagnetic behaviour for BCC Mn were they to exist at low temperatue. This is in agreement with previous results for γMn (Arrott 1966; Asano 1973), but is a new result for δMn.

The pole in the γ phase is related to nesting portions of the Fermi surface which build up a maximum near $(a/2\pi)q = 0{\cdot}67$ as a band 5 'humming bird' enters a band 4 'nest'. Incidentally there are eggs in band 3. Upon enhancement a pole occurs at the same q value, predicting incommensurate antiferromagnetism for pure γMn. Experimentally a tetragonal distortion occurs below the Neel temperature, T_N: FCC alloys of Mn and Cu become commensurate FCT (tetragonal) antiferromagnets according to neutron diffraction studies, up to 85% Mn, where the structure becomes unstable with respect to the αMn phase.

The product $I \times D(E_F)$ is greater than 1 for BCC Mn as a consequence of the density of states which is 50% higher than for FCC Mn. This product is comparable to the corresponding product in BCC Fe, and produces a negative uniform susceptibility, an occurrence used by Stoner (1939) and more recently by Janak (1977) to predict ferromagnetism. The negative enhancement at $q = 0$ is interpreted in a similar fashion here for BCC Mn. The pole for $q \neq 0$ is a consequence of the form of the theory and is guaranteed if $\chi(0) < 0$, since $\chi_0(q)$ approaches zero for q large enough.

Since δMn occurs between 1407 K and 1518 K, which is well above the expected Neel temperature, direct verification of its ferromagnetism is not possible (the present work has assumed zero temperature). However it may be possible to observe the magnetic phases at high pressure, in quenched or alloy stablised BCC Mn, or in epitaxially grown BCC Mn layers (Arrott 1987). Since spin excitations have been observed in other magnetic transition metals well above the transition temperature, they may still persist in the γ and δ phases of Mn. High temperature neutron diffraction studies of Mn are in order.

The conclusions about magnetism in Mn are based upon a specific band structure calculation (Papaconstantopoulos 1986). A total energy calculation to determine the equilibrium low temperature lattice constant is under way, as well as band calculations of the assumed ferromagetic phase to search for a magnetic moment.

4. Conclusion

In conclusion, the results of this paper are summarised as follow:

(1) A self-consistent local-density correction has been applied to the RPA susceptibility for the wave-vector dependence of $\chi(q)$ for transition metals near Cr.

(2) Although approximations were necessary, *no adjustable parameters were introduced.*

(3) The wave vector of the spin density wave in Cr is correctly predicted from the pole of $\chi(q)$.

(4) FCC Mn is an incommensurate antiferromagnetic and BCC Mn is ferromagnetic at $T = 0$ K.

(5) A search for spin excitation of (δ, γ)-Mn might prove successful, and by appropriate growth it should be possible to produce ferromagnetic or antiferromagnetic layers or alloys of Mn.

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