Helvetica Physica Acta,
Vol. 56 (1983) 117-130
0018-0238/83/010117-14$1.50+0.20/0

MAGNETIC CORRELATIONS IN METALLIC MAGNETICS AT FINITE TEMPERATURES.

K.R.A. Ziebeck*, P.J. Brown*, J. Déportes†, D. Givord†, P.J. Webster†† and J.G. Booth††.

* Institut Laue-Langevin, 156X Centre de Tri, 38042 Grenoble Cedex, France.

† Laboratoire Louis-Néel, CNRS, 166X, 38042 Grenoble Cedex, France.

†† Department of Physics, University of Salford, Salford M5 4WT, England.

Although the ground state properties of transition metal magnets are reasonably well described by band theory their finite temperature properties are not. In contrast to magnetic insulators and rare earth metals, where well localised magnetic moments exist due to localised electrons, the magnetism of itinerant systems (3d transition metals and some of their compounds) is carried by electrons with delocalised wavefunctions participating in the Fermi surface. The itinerant nature of the "magnetic" electrons leads to a strong coupling between translational degrees of freedom (hopping processes) and magnetic degrees of freedom. Discussion of magnetic degrees of freedom alone (e.g. by a Heisenberg-type Hamiltonian) as is possible for localised magnetism is not appropriate. In spite of recent theoretical progress there exists considerable controversy as to what kind of fluctuations are responsible for driving the paramagnetic phase transition and about the nature of the paramagnetic phase itself. Paramagnetic neutron scattering provides a powerful tool for probing magnetic fluctuations in the paramagnetic state and is sensitive to the wave vector dependent features which distinguish different current theories. This sensitivity has been exploited in studying the spin density-spin density correlation function in a wide range of transition metal paramagnets. Polarised neutrons and polarisation analysis have been employed in order to obtain a clear measurement of the paramagnetic scattering and its magnitude.

The results of these measurements show that the paramagnetic properties of transition metals e.g. Fe, Ni, etc. are dominated by strong ferromagnetic correlations extending over several lattice spacings. They indicate how, by means of spatial correlations, local exchange splitting of an itinerant 3d band may be maintained in the magnetically disordered phase and explain the large values of "effective" moments obtained in susceptibility measurements. In the case of iron and nickel the spatial correlations enable short wave length spin waves to propagate above T_c. The spatial correlations observed in the present neutron experiments demonstrate the coherent nature of the wavefunctions characterising the "magnetic" itinerant electrons.

INTRODUCTION

Numerous measurements now exist, de Haas van Alphen, neutron diffraction, transport, galvano-magnetic, etc. which indicate that the ferromagnetism of iron is carried by d electrons participating in the Fermi surface. Band theory accounts satisfactorily for the ground state properties of iron and notably for the non-integral moment of 2.216 μ_B per atom. It should be emphasised that this moment which may be obtained either from neutron or magnetisation measurements is not a local moment in the sense of that occurring in systems on the insulating side of the Mott transition. The ground state properties of insulating magnets are generally well accounted for by Heisenberg models in which the magnetic electrons have localised wavefunctions. Thermal fluctuations of the magnetisation density occur in the form of collective excitations, spin waves, having energies less than $\sim(KT_c)$ i.e. typically < 0.05 eV. The thermal fluctuations i.e. spin waves can exist for all wavevectors whilst the amplitude of the moment remains fixed. The magnetism of these systems can thus be discussed by considering just the magnetic degrees of freedom. They may be classified as narrow band materials for which the exchange energy is substantially greater than the band width (negligible overlap of the d functions).

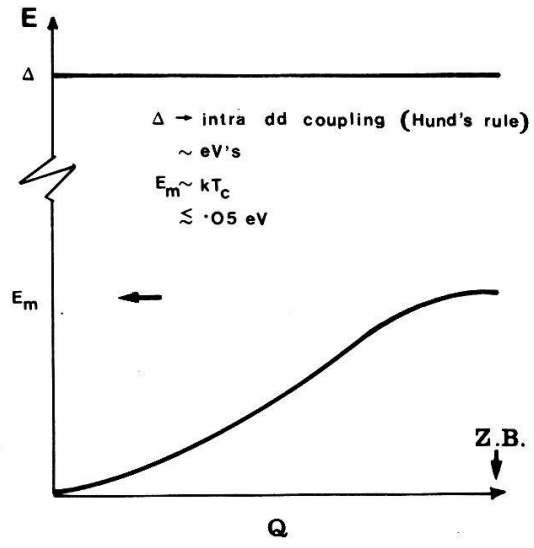

Fig. 1. Spectrum for spin waves and single particle excitations in a narrow band system.

The magnetism in iron and other pure transition metals is carried by itinerant electrons having at least partially delocalised wave functions. It is the fact that these electrons participate in the Fermi surface which distinguishes itinerant magnetism from localised behaviour. The itinerant nature of the "magnetic" electrons leads to strong

coupling between translational degrees of freedom (hopping processes) and magnetic degrees of freedom, so that a consideration of the magnetic degrees of freedom alone, e.g. using a Heisenberg Hamiltonian, is not adequate. Owing to the delocalised nature of the d electrons they move through the lattice with a kinetic energy characterised by the band width, which for transition metals is $\sim$5 eV. Thus the excitation spectrum of the single particle depends on details of the band structure.

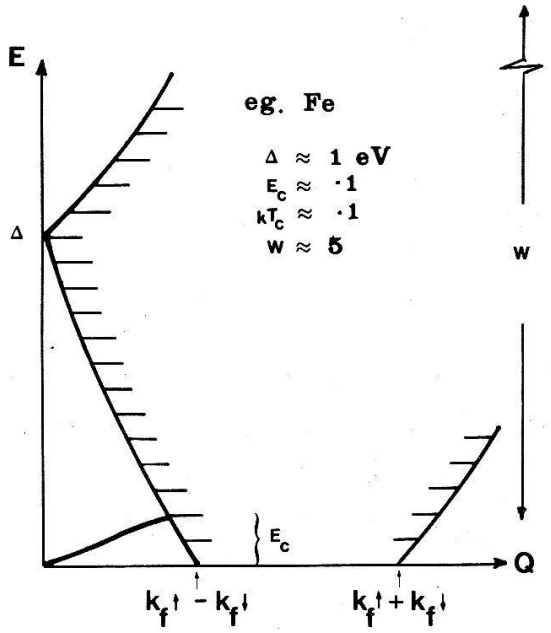

Fig. 2. Spectrum for spin waves and single particle excitations in an itinerant magnet.

GROUND STATE

Inelastic neutron scattering measurements [1] reveal the presence of spin waves, coherent motion of electron-hole pairs, which at small wave vectors disperse isotropically with a stiffness constant of D = 230 meV Å^2 ($\omega = Dq^2$). At high energy transfers corresponding to $\sim$100 meV the spin wave intensity was found to decrease anomalously by an order of magnitude (see Fig. 3). Towards the zone boundary there are no well defined features in either wave vector or energy. The single particle spin flip fluctuations give rise to an extremely low level of scattering which extends over phase space and are predicted to extend up to the band width. Whereas the collective excitations are confined to a small volume of reciprocal space around the zone centre. It must be emphasised that the intensity associated with the spin

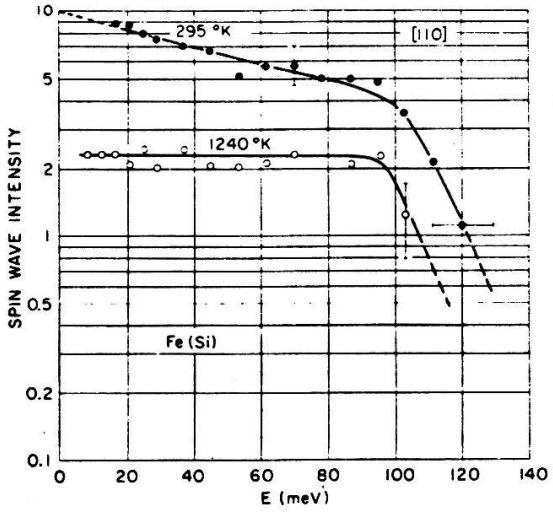

Fig. 3. Spin wave intensity versus energy in the (110) direction of $Fe_{88}Si_{12}$ [1].

waves is vastly inferior to that corresponding to the Bragg scattering, centred at q = 0. The abrupt reduction in the spin wave intensity corresponds to their entry into the single particle continuum. At this wave vector and energy it becomes as easy to excite an electron from the majority to the minority band as to create a spin wave. Quantitative calculations of spin waves in d metals based on calculated band structures are in reasonable agreement with the results of inelastic neutron scattering.

FINITE TEMPERATURES

At finite temperatures Stoner theory is less successful since the average amplitude of the local spin density is predicted to decrease with temperature until it vanishes at $T_c^{Stoner} \sim 10,000$ K for iron. Only single particle spin flip excitations are considered to drive the ordered to paramagnetic phase transition and the Curie temperature is vastly over-estimated, T_c experimental 1044 K. Thus fluctuations of the spin density having a lower characteristic frequency $\sim (KT/h)$ must dominate in defining the transition temperature. In localised systems the paramagnetic phase is established by the thermal disorder of atomic spins of fixed amplitude. Over the years considerable experimental evidence has accumulated to suggest that the magnetic behaviour of iron falls between the extremes of the Heisenberg and the Stoner models, and that the moment does not collapse at T_c. The thermal variation of the static susceptibility and resistivity measurements and the

absence of a significant magneto volume change at T_c [2] suggests the persistence of an exchange splitting above T_c. In iron, as in many transition metal magnets above T_c, the uniform static susceptibility roughly follows a Curie-Weiss law, in contradiction with Stoner theory. It has been shown recently that rotations of the "local" moments (transverse fluctuations) in iron, can destroy long range order at temperatures consistent with the observed values of T_c [3,4]. This mechanism has similarities to localised systems as described by Heisenberg models, but with detailed differences due to the itinerant nature of the electrons. These assertions are supported by inelastic neutron scattering measurements of spin waves at high temperatures [1].

The neutron measurements reveal that the spin waves remain well defined and are only slightly renormalised up to T_c (Fig. 4). Furthermore the wave vector and frequency at which the spin waves enter the Stoner continuum does not change significantly with temperature, indicating that the band structure or more precisely the exchange splitting does not change significantly with temperature. At small wave vectors i.e. < 0.3 $Å^{-1}$ the collective excitations become over critically damped at T_c and the response in this region is entirely diffusive in character. A further important discovery is the persistence of spin wave scattering above T_c beyond 1.4 T_c. Therefore not only must a moment exist above T_c but also a considerable degree of spatial order. The fact that spin waves propagate for wave lengths shorter than $\lambda_c = 2\pi/Q_c$ where Q_c is 0.3 $Å^{-1}$ suggests that the spin density remains correlated over distances of 15-20 Å above T_c, in agreement with the fluctuating band theory of itinerant magnetism [3,4,5,6,7]. This theory is based on very strong short range magnetic order existing well

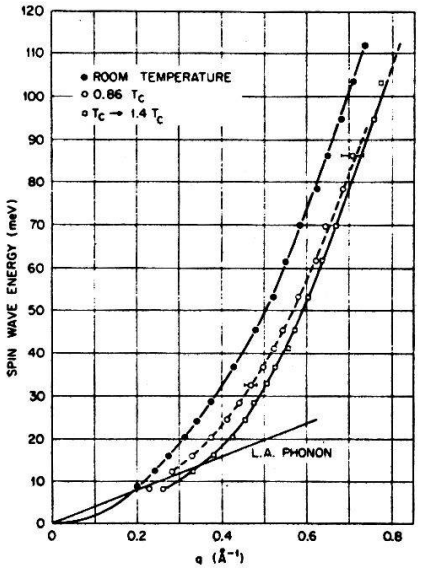

Fig. 4. Spin wave dispersion in $Fe_{88}Si_{12}$ [1].

above T_c due to the phase coherence of electronic wave functions over distances considerably larger than the interatomic spacing. Although the observed spin waves remained well defined above T_c, their intensity was found to have dropped significantly, with the low frequency modes affected most.

The general features of the inelastic neutron scattering measurements have been accounted for using the fluctuating band theory. However, models based on a modified Heisenberg Hamiltonian e.g. Zener model [8,9], are unable to reproduce the spin wave peaks observed in constant 'q' plots. These and other theories describe the paramagnetic phase as a random arrangement of spin up and spin down electrons (treated with CPA-like methods [10]) with practically no short range order outside the direct vicinity of T_c.

PARAMAGNETIC STATE

From the above discussion it is clear that a direct measurement of the spin density-spin density correlation function can provide a powerful means of distinguishing the domains of applicability of different models. Such a measurement can be obtained using polarised neutrons and polarisation analysis to obtain a clean separation of the paramagnetic neutron scattering cross-section. This is possible because only the magnetic part of the scattering is sensitive to the angle between the neutron polarisation and the scattering vector. The difference between the spin flip cross-sections for neutrons polarised parallel and those perpendicular to the scattering vector may be related to the magnetic response function $S(Q,\omega)$ [11]

$$\left(\frac{d^2\sigma^{+-}}{d\Omega d\omega}\right)_{||} - \left(\frac{d^2\sigma^{+-}}{d\Omega d\omega}\right)_{\perp} = \frac{\gamma r_o}{3} \frac{V}{V_c} N_m S(Q,\omega) \qquad (1)$$

where V is the volume of the sample, V_c the volume of the unit cell, N_m the number of magnetic atoms per unit cell, r_o is the classical electron radius and γ the magnetic moment of the neutron. The measured paramagnetic scattering can then be expressed in terms of the correlation function $M^2(Q)$ given by

$$M^2(Q)\ f^2(Q) = \int_o^{E_i} S(Q,\omega)\ \delta E \qquad (2)$$

in which f(Q) is the form factor of the magnetic carriers. The scattering function $S(Q,\omega)$ of a Heisenberg magnet when integrated over all relevant frequencies and summed throughout the zone becomes:

$$\frac{1}{g^2\mu_B^2}\,\Sigma_Q \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\Sigma_\alpha\, S^{\alpha\alpha}(Q,\omega) = NS^2 + NS = NS(S+1) \quad (3)$$

The S^2 term represents the Bragg scattering component and the term linear in S represents zero point motion, diffuse scattering, etc. The sum rule is valid at all temperatures both in the ground and paramagnetic state. Thus the difference in the diffuse scattering between the ordered and disordered phases comes from the S^2 component.

The validity of this sum rule has been verified for the localised metallic ferromagnet Pd_2MnSn (T_c = 189 K). In this material only the manganese atoms carry a moment and are separated by 4.5 Å; thus there is negligible overlap of the d functions giving rise to the moment. Thermal fluctuations of the moment outside of the ground state i.e. spin waves occur throughout the zone [12] and are well described by Heisenberg theory. The spin waves are strongly renormalised with temperature and disappear close to T_c. Above T_c the paramagnetic response [13] is wave vector independent after correction for the atomic form factor f(Q), thus indicating the absence of spatially dependent correlations between spins on different sites (Fig. 5). The observed correlation function $M^2(Q)$ is determined by the self correlations giving $M^2(Q) = g^2\, S(S+1)$. Thus the paramagnetic phase of Pd_2MnSn can be visualised as consisting of randomly aligned atomic spins of fixed amplitude.

It is difficult to visualise a similar paramagnetic state in itinerant magnets. Paramagnetic scattering measurements on both single crystals and polycrystalline samples of pure [14] and Fe + 5 At.%Si [15] (stabilised α phase) enable both the spatial correlations and the temporal evolution of electron spins to be investigated. The paramagnetic scattering observed at four different temperatures for scans made in the (110) direction in a sample of Fe - 5At.%Si is shown in Figure 6. The observed paramagnetic scattering is peaked in the forward direction and around

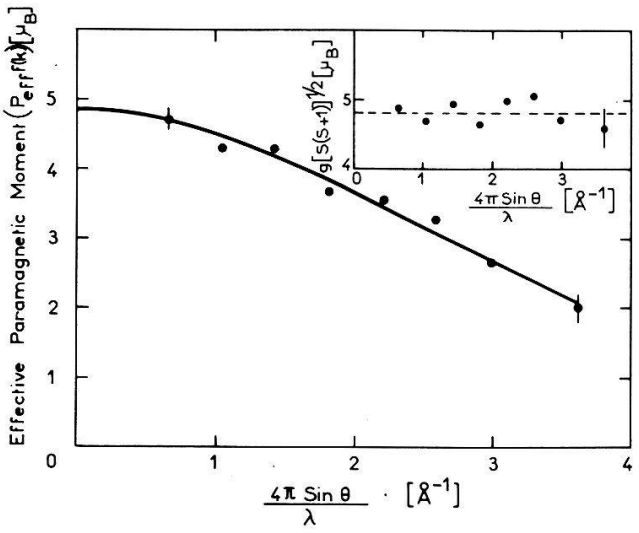

Fig. 5. Paramagnetic scattering in Pd_2MnSn at 4 T_c.

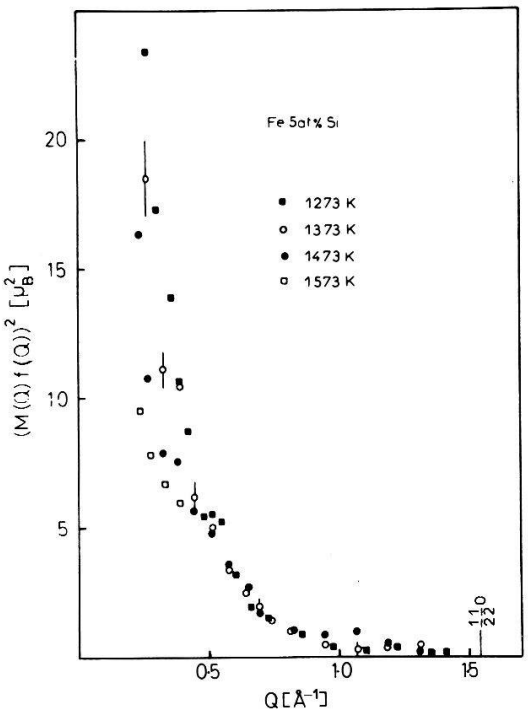

Fig. 6. Paramagnetic scattering along the (110) direction in Fe - 5 At.% Si.

nuclear Bragg peaks. Such behaviour may be expected if there exists spatial correlations of a predominantly ferromagnetic nature In the Heusler, Pd_2MnSn, only the self correlation $\langle M_i M_j \rangle$ for i = j where i and j are the site labels contribute to the scattering In iron both self and spatial correlations $i \neq j$ give rise to paramagnetic scattering. Measurements made in the (001) and (111) directions gave rise to a slightly larger level of scattering than in the (011) direction, but within the experimental error and in comparison with the data observed with the polycrystalline samples the scattering is essentially isotropic. Significant thermal variation of the scattering is observed only for wave vectors less than ~ 0.4 Å^{-1}. This scattering arises from the residual long range order and is found in all paramagnets close to the transition temperature. Spooner and Averbach [16] have investigated this scattering using unpolarised neutrons and have shown that the Ornstein-Zernicke approximation gives a reasonable account of the observed scattering i.e. $1/r \exp - r/\xi$. However this functional form was found to break down for distances corresponding to

15 - 20 Å. This distance corresponds to a wave vector of 0.4 $Å^{-1}$, beyond which the polarised neutron measurements indicate that the correlations giving rise to the enhanced scattering are essentially temperature independent. These correlations which characterise the short range magnetic order are found only in itinerant magnetism and reflect the delocalised nature of the d wave function. For wave vectors greater than 0.9 $Å^{-1}$ out to the zone boundary there is a low level of observed scattering. Constant Q scans performed close to the zone boundary revealed that this low level of scattering persisted beyond 100 meV. The absence of significant scattering at large wave vectors is in stark contrast to the prediction of the Heisenberg model. Similar behaviour has been observed in the paramagnetic phase of nickel [7]. Constant Q scans carried out at wave vectors corresponding to the region of short range order i.e. $0.4 < Q < 0.9$ $Å^{-1}$ reveal that the scattering is concentrated at low energy transfers. Thus the neutron scattering experiments effectively integrate over all the thermal fluctuations which are well defined in Q and ω. The absence of significant scattering at large wave vectors effectively demonstrates the existence of short range magnetic order. It is interesting to note that the original measurements of paramagnetic scattering from iron [16] using unpolarised neutrons and no energy analysis have a Q dependence which falls off more rapidly than expected for 3d electrons in a localised model.

The observed scattering may be integrated throughout the zone to obtain an "effective" amplitude. In an "itinerant" system there may be no well defined energy gap between the thermal fluctuations (transverse modes) and the quantum fluctuations (longitudinal modes). In the absence of such an energy gap the "effective" atomic moment is not well defined and may vary strongly according to the averaging time of the experiment from which it is derived. We therefore wish to distinguish the moment we derive from paramagnetic scattering experiments on itinerant systems from that observed in local systems and from that obtained in the ground state, since it is not possible to distinguish between the thermal and quantum fluctuations. Thus we define the "on site correlation amplitude" OSCA as

$$\langle M_i M_j \rangle \propto \int^{K_o} Q^2 M^2(Q) \frac{\text{Sin } QR}{QR} dQ \qquad (4)$$

for $i \neq j$

$$M_i^2 \propto \int^{K_o} Q^2 M^2(Q)\, dQ \qquad (5)$$

The phase space factor gives a large weight to the large Q components. Although it is possible to Fourier transform the observed data using Eq.(4) [17,18], the resulting transform depends substantially on the large Q components which are hardly significant and have a large error after multiplication by Q^2. The resulting transform gives a correlation length of between 6 - 10 Å. However the Fourier transform does not contain more information than is contained in $M^2(Q)$ and it is more instructive to plot $Q^2M^2(Q)$ versus Q since this indicates which Fourier components contribute significantly to the OSCA. In Figure 7 it may be seen that the

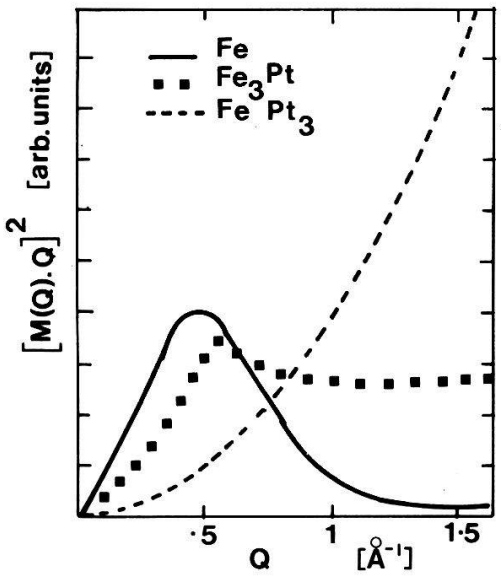

Fig. 7. $Q^2M^2(Q)$ v. Q for αFe, Fe_3Pt and Pt_3Fe.

dominant Fourier components giving rise to the on-site correlation function are $\lambda_c = 2\pi/Q_c \approx 16$ where $Q_c = 0.4$ Å^{-1}. Both the characteristic wavelength and OSCA were found to be essentially temperature independent up to at least 1.5 T_c, suggesting that band structure, particularly the exchange splitting does not change significantly over this temperature range. However the OSCA, determined from the scattering which is well defined in both Q and energy, is substantially less than the ground state moment.

The reduction corresponds to approximately one third of the scattered intensity.

The separation of quantum and thermal fluctuations has been dealt with in MnSi [19], in which it was possible to integrate over the band width and then subtract the quantum fluctuation by repeating the measurements close to the ground state i.e. below T_c. In this manner the amplitude associated with the manganese atoms was found to increase slightly whereas measurement in the paramagnetic phase up to 20 T_c and including quantum fluctuations suggested a substantial increase. Similar experiments on iron are not at present feasible since the band width is approximately 5 eV, but the possible effect of the quantum fluctuations in determining OSCA may be understood by considering the time average of the magnetisation density - magnetisation density correlation function $M^2(Q)$. Consider the response of electron spins to a perturbation of frequency $\Delta\omega$, then the states that can be excited by an energy transfer $\hbar\Delta\omega$ have a momentum spread ΔK given by $\Delta K = \Delta\omega m^*/\hbar K_f$ where m^* is the effective mass of electrons at the Fermi surface and K_f their Fermi wave vector. The corresponding wave packet has an extent in real space Δx given approximately by the uncertainty principle

$$\Delta x \sim \frac{\hbar K_f}{\Delta\omega m^*} = \frac{1}{\Delta K} \qquad (6)$$

Therefore the effect of omitting the high frequency response in the evaluation of $M^2(Q)$ is to average the correlation over a distance Δx given approximately by Eq.(6) above. An upper limit for the distance involved can be obtained by observing that the band width W is given by

$$W = \frac{\hbar^2 K_f^2}{2m^*} \quad \text{with} \quad K_f = \frac{\pi}{a} \qquad (7)$$

and a is the interatomic distance. The maximum distance is of the order $W/\hbar\Delta\omega$ times the interatomic distance. In an ionic material or an intermetallic compound e.g. Pd_2MnSn in which the d band is narrow, the factor $W/\hbar\Delta\omega$ may be of order unity for the energy resolution of the experiment ($\hbar\Delta\omega \sim E_i \sim 28$ THz). In such

a case the paramagnetic scattering experiment will measure the full unpaired moment per atom. For iron the width of the d band is $\sim$5 eV (1 eV $\sim$ 242 THz) so the average is over many unit cells. If the averaging distance is greater than the correlation length (λ_c) of the paramagnetic excitations the measured moment per atom (OSCA) will be less than the mean unpaired moment per atom within the correlated region. This may be demonstrated experimentally by comparing results obtained on Fe, Fe_3Pt [21] and $FePt_3$ [22]. With increasing Pt content, the d overlap of the iron atoms becomes less with a corresponding decrease in the band width. In the ground state transverse fluctuations of the magnetisation density occur progressively throughout the zone with increasing Pt content. This is reflected in the paramagnetic scattering by an increasing importance of the large Q component to the Fourier spectrum. Eventually in Pt_3Fe all the Fourier components contribute in establishing $M^2(Q)$.

CONCLUSIONS

Neutron scattering measurements confirm that the exchange splitting in iron and other itinerant magnets persists beyond T_c into the paramagnetic phase. Measurements both close to the ground state and in the paramagnetic phase demonstrate the importance of quantum fluctuation which in the case of itinerant magnets are not distinct from the thermal fluctuations. Inelastic neutron scattering measurements close to the ground state indicate that the transverse fluctuations of the magnetisation density are confined to a small value of reciprocal space. Furthermore, measurements made above T_c indicate that the region of spin wave fluctuations remains unchanged. These results are consistent with the predictions of band theory which also suggests the presence of a low level of scattering towards the zone boundary and extending up to the band width. The absence of significant scattering towards the zone boundary has been confirmed by paramagnetic neutron scattering measurements in both iron and nickel. These fluctuations have the same origin as those characterising the static susceptibility in the paramagnetic phase of chromium. Above the Néel temperature the static susceptibility of chromium increases

slowly with temperature and is characterised by fluctuations close to the Fermi level i.e. Pauli paramagnetism $\propto T/T_F$. Apart from the zone centre, polarised neutron scattering measurements [23] on paramagnetic chromium indicate a low level scattering characteristic of a single electron response. These results demonstrate the inadequacies of the Heisenberg model in which the amplitude of the spin density remains fixed and all Q components contribute to the paramagnetic response. However the local band model and Moriya's unified theory which includes a wave vector cut-off for the spin fluctuations are in reasonable agreement with most of the experimental results on itinerant magnets. These theories have the advantage that they are based on band theory which already accounts for the ground state properties. The spatial correlations stabilise the exchange splitting above T_c and enable spin waves to propagate in the paramagnetic phases of iron and nickel. As the overlap of the d functions decreases, for example by alloying, spin waves propagate progressively across the zone in the ground state. Thus in the paramagnetic phase the large wave vector components of the spin fluctuations become increasingly important as the band width decreases. In the limit of negligible overlap, e.g. as in Pd_2MnSn, the Heisenberg model becomes applicable.

Acknowledgements

We are grateful to Professor T. Moriya for many helpful communications and to A. Perkins for Technical assistance.

REFERENCES

[1] Lynn J.W. Phys. Rev. B11 (1975) 2624;
Lynn J.W. and Mook H.A. B23 (1981) 198.

[2] Shiga M. Inst. Phys. Conf. 55 (1981) 241.

[3] Capellmann H. Z. Phys. B34 (1979), and
J. Phys. F4 (1974) 1466.

[4] Korenmann V., Murray J.L. and Prange R.E. Phys. Rev. B16 (1977) 4032, 4048, 4058.

[5] Capellmann H. and Veira V. Phys. Rev. B25 (1982) 3333, and

Solid State Comm. 43 (1982) 747.

[6] Moriya T. J. Phys. Soc. Japan 51 (1982) 2806, and J. Mag. Magn. Mat. 14 (1979) 1.

[7] Proceedings of the ICM Conference, Kyoto 1982, J. Mag. Magn. Mat. 31-34 1983.

[8] Edwards D.M. J. Phys. F12 (1982) 1789.

[9] Sriram Shastry B., Edwards D.M. and Young A.P. J. Phys. C14 (1981) L665.

[10] Hasegawa H. J. Phys. Soc. Japan 46 (1979) 1504.

[11] Ziebeck K.R.A. and Brown P.J. J. Phys. F10 (1980) 2015.

[12] Noda Y. and Ishikawa Y. J. Phys. Soc. Japan 40 (1976) 699.

[13] Ziebeck K.R.A., Webster P.J., Brown P.J. and Bland J.A.C. J. Mag. Magn. Mat. 24 (1981) 258.

[14] Brown P.J., Capellmann H., Déportes J., Givord D. and Ziebeck K.R.A. J. Mag. Magn. Mat. (in press).

[15] Brown P.J., Capellmann H., Déportes J., Givord D. and Ziebeck K.R.A. J. Mag. Magn. Mat. 30 (1982) 243.

[16] Spooner S. and Averbach B.L. Phys. Rev. 142 (1966) 291.

[17] Wilkinson M.K. and Shull C.G. Phys. Rev. 103 (1956) 516.

[18] Capellmann H. J. Mag. Magn. Mat. 28 (1982) 250.

[19] Edwards D.M. to be published.

[20] Ziebeck K.R.A., Capellmann H., Brown P.J. and Booth J.G. Z. für Physik 48 (1982) 241.

[21] Ziebeck K.R.A., Webster P.J., Brown, P.J. and Capellmann H. J. Mag. Magn. Mat. (in press).

[22] Ziebeck K.R.A., Webster P.J., Brown P.J., Johnson S.M. and Mankikar R.M. to be published.

[23] Ziebeck K.R.A., Booth, J.G., Brown P.J., Capellmann H. and Bland J.A.C. Z. Phys. B48 (1982) 233.