Positron annihilation study of the Fermi surface of Ni$_2$MnGa

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Abstract. The Fermi surface of the ferromagnetic shape-memory alloy Ni$_2$MnGa has been determined experimentally with two-dimensional angular correlation of electron–positron annihilation radiation. Our results are supported by first principles electronic structure calculations. The measured electron occupancy within the Brillouin zone is consistent with the existence of two nesting features present in the Fermi surfaces calculated in previous studies. The nesting vectors of the calculated Fermi surface match the modulation of the pre-martensitic intermediate structure and that of the martensitic structure.

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1. Introduction

Actuator materials with large strains, appreciable thrust and rapid response times would have widespread technological applications. Ni$_2$MnGa has potential for such applications because it is one of very few metals that undergo a martensitic transformation (MT) within the ferromagnetic phase [1]. This enables the redistribution of martensitic domains on the application of a magnetic field which produces greater strains, and hence actuator response, than magnetostrictive materials such as rare-earth alloys [2–4].

An MT is a displacive, diffusionless structural phase transition between a high temperature, high symmetry phase and a low temperature phase with less symmetry. Such a transition is responsible for the properties of shape-memory and superelasticity of alloys such as Ni–Ti that are used in a wide variety of applications [5]. Heating and cooling through an MT is often too slow for non-magnetic shape-memory materials to be used as actuators. This has led to an intense search for and development of materials, such as Ni$_2$MnGa, where structural changes can be induced by an external magnetic field [2]. Stoichiometric Ni$_2$MnGa is ferromagnetic below $T_C \sim 380 \text{ K}$ and undergoes a transition from the cubic L2$_1$ phase to a modulated tetragonal structure with $c/a = 0.97$ at $T_M \sim 220 \text{ K}$ [1, 6].

The achievement of field-induced strains in Ni$_2$MnGa [2] has occurred in spite of the absence of an established microscopic understanding of the MT in Ni$_2$MnGa, and indeed in other shape-memory alloys. In the pursuit of such a theory, much experimental and theoretical effort has focused on precursor phenomena that are observed as the MT temperature is approached from above. Inelastic neutron scattering reveals softening of the TA$_2$ branch of the phonon dispersion along the $[\xi, \xi, 0]$ direction that becomes stronger with decreasing temperature [7]. As temperature decreases the softening evolves into a well-defined minimum in the dispersion at $\xi = \frac{1}{3} \frac{2\pi}{a}$. Before the frequency of this minimum reaches zero, the system undergoes a weak first order phase transition (at a temperature between 247 and 260 K) to an intermediate or pre-martensitic (PM) phase in which the cubic structure has a periodic transverse modulation with the wavevector of the soft phonon [6, 8]. The transition temperature is very sensitive to sample stoichiometry. In the PM phase, the symmetry of the crystal remains cubic but the atoms assume modulated positions with a nearly six-plane period along...
the [110] direction, associated with a phonon anomaly in the TA branch at the wavevector \( \mathbf{q}_{\text{PM}} = \left[ \frac{1}{3} \pm 0 \right](2\pi/a) \). A number of martensitic (M) structures have been reported for \( \text{Ni}_2\text{MnGa} \), including both a commensurate modulation with a seven unit cell periodicity (and thus known as 7 M) [9], and an incommensurate modulation with a periodicity of nearly five planes (known as 5 M) [6, 10]. Further modulations may also be accessed via the application of compressive and tensile stress [11]. Brown et al [9] argue that the 5 M phase was observed due to the presence of internal stress within the samples studied, and that the true 7 M structure can only be observed in a highly-ordered stoichiometric sample. These studies clearly establish the modulations assumed in the Martensitic phase of \( \text{Ni}_2\text{MnGa} \) to be sample dependent.

Early calculations [12, 13] suggested that the MT had its origins in the band Jahn–Teller effect, a view which has certainly found experimental support in hard x-ray photoemission in \( \text{Ni}_2\text{Mn}_{1-x}\text{Sn}_{x} \) [14]. Those authors were able to track the 3d \( e_g \) minority band states towards the Fermi level, concluding that the Jahn–Teller splitting has an important role in the structural instability of the cubic phase. It is important to note that not all ferromagnetic shape-memory alloys have Fermi surfaces with as strong nesting as \( \text{Ni}_2\text{MnGa} \) (for example, \( \text{Co}_2\text{NiGa} \) has an MT, but shows neither phonon softening nor Fermi surface (FS) nesting [15]), and while it would certainly be wrong to conclude that nesting is an essential ingredient in the MT, it would be equally wrong to claim that it plays no part in \( \text{Ni}_2\text{MnGa} \). For further discussion of this, see [16].

A proposed microscopic origin of the PM behaviour is electron–phonon coupling in conjunction with a strongly nested FS [6]. Theoretical studies have previously identified nesting features in calculated FSs with PM behaviour in \( \text{Ni-Al} \) [17] and \( \text{NiTi} \) [18]. Electronic structure calculations of the cubic phase of \( \text{Ni}_2\text{MnGa} \) reveal peaks in the generalized susceptibility and FS nesting features with the correct wavevectors to be possible causes of PM behaviour [19] and the modulation of the M phase [20]. First principles calculations [21–23] of the phonon dispersion reproduce anomalies observed in experiments, these authors attributing many of the instabilities to the presence of FS nesting.

Velikokhatnyi and Naumov [20] were the first to point to FS features as a possible driving force. Although they were unable to identify any features in the FS which could explain the PM modulations, they did find nesting at a vector which was close to that of the 5M phase. Subsequently, Lee et al [19] pointed out that the PM transition occurs at finite temperature (and at an unsaturated magnetization), and by treating temperature effects on the spin-polarized bands in a Stoner-like mean-field manner they were able to track the evolution of the FS nesting features as the spin moment is reduced by the finite temperature. They found that although the FS at saturation spin-polarization did not exhibit nesting at the \( \mathbf{q}_{\text{PM}} \) vector, it did at the moment corresponding to that observed at the PM transition temperature [24]. Further investigation by Bungaro et al [21] revealed strong electron–phonon coupling along with soft phonons, and the authors went on to attempt to identify nested parts of the FS. However, no checks were made on the real part of the generalized susceptibility to look for singular behaviour at the appropriate vectors [25]. In a comprehensive and challenging first-principles study [26], Uijttewaal et al were able to show that the magnons stabilize the austenitic phase at higher temperatures, with magnetic fluctuations being involved in the PM behaviour and both vibrational and magnetic fluctuations driving the MT.

Although direct experimental measurement of the FS has so far been lacking, a number of recent experiments have provided support for the theoretical predictions. By performing a neutron scattering experiment, Shapiro et al [27] were able to observe well-defined phasons in the M phase, a signature of a 3D charge-density-wave phase, and expected to occur due

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to the predicted FS nesting. Further evidence for the presence of FS nesting was provided by Opeil et al [28], whose ultra-violet photoemission measurements revealed the opening of a pseudogap below the Fermi level at the PM transition, and associated with the gapping of part of the FS.

In this paper we present a positron annihilation measurement of the FS of Ni$_2$MnGa in the ferromagnetic state above the PM transition.

2. Positron annihilation and the measurement of the Fermi surface

The study of the electronic structure of crystalline materials, and specifically metallic systems, has formed the backbone of physics in the solid state, not least because of their technological importance. The quest to understand the nature of the metallic state has required a close alliance of theory and experiment. Our vision of the electronic ground state of a metallic system is dominated by the concept of the FS, dictating many of the transport and magnetic properties. The importance of knowing the FS topology of a metallic system cannot be overestimated, as illustrated by the accumulation of an arsenal of FS probes, including quantum oscillatory techniques [29, 30], angle-resolved photoemission [31] and Compton scattering [32, 33].

However, the applicability of quantum-oscillatory techniques is normally restricted to low temperature phases (although in favourable circumstances it can be applied at higher temperatures, as shown by Goddard et al in the shape-memory alloy AuZn [34]) and to high purity samples, and photoemission relies on the surface being representative of the bulk. Thus the investigation into the FS topologies of bulk disordered systems (such as substitutional alloys), high temperature phases (such as above the MT in Ni$_2$MnGa), or even precipitates [35, 36], is often excluded. It is in these regimes that positron annihilation experiments can make significant novel contributions.

Positrons are a powerful probe of the electronic environment in a sample. For FS studies, significant information can be derived from measurements of the $\gamma$-photons emanating from the electron–positron annihilation in the sample being studied in an experiment known as two dimensional angular correlation of positron annihilation radiation (2D-ACAR). It is the measurement of the angular deviations from anti-collinearity of the two $\gamma$-photons that supplies two of the momentum components of the electron–positron pair immediately before annihilation. Relying only on the conservation laws of energy and momentum, the positron technique is not restricted to low temperature and ordered phases, providing an invaluable window on the electronic structure of room temperature phases and disordered alloys. A 2D-ACAR experiment provides a projection (or integral over the one unresolved component) of the underlying three dimensional (3D) electron–positron momentum density. This momentum distribution contains information about the occupied regions of reciprocal space, and hence about the FS.

There are, however, two principal caveat to be borne in mind when interpreting the experimental results. Firstly, the difference between the electron and electron–positron momentum density is not trivial, and in certain situations the task of extracting FS information is hampered by the effects of the perturbative (as far as fermiology is concerned) positron wave-function (although recent work has tackled this directly [37]). Secondly, the data are a 2D projection of the 3D momentum density, with all the associated complications due to the superposition of features, and the problem of recovering the 3D density is tackled in a later section.
The application of the 2D-ACAR technique to a more complex range of specimens has demanded a parallel escalation in the sophistication of the data analysis tools, ranging from Maximum Entropy deconvolution [38] through to fitting procedures [39]. These tools and others which have been conceived, implemented and developed in various groups around the world, have heralded a new era of 2D-ACAR analysis commensurate with the increasing electronic complexity of the systems being studied.

Since the momentum density technique is \( k \)-resolved, it can provide a view of the shape of the FS directly, and thus is ideal for probing the propensity towards nesting which is thought to play a role in phenomena including magnetic ordering in the heavy rare-earths [40–43], compositional short range order [44], and, of course, the electron-phonon interaction [45–47] which is the key to understanding conventional superconductivity and the lattice instabilities associated with the shape-memory effect.

2.1. Theoretical background

A 2D-ACAR measurement yields a 2D projection (integration over one dimension) of an underlying two-photon momentum density (TPMD), \( \rho^{2\nu}(\mathbf{p}) \). This can be expressed as:

\[
\rho^{2\nu}(\mathbf{p}) = \sum_{\text{occ.}, j, k} \left| \int \! \! \! \int d\mathbf{r} \sqrt{\gamma(\mathbf{r})} \psi_{k,j}(\mathbf{r}) \psi_{+,\mathbf{p}}(\mathbf{r}) \exp(-i \mathbf{p} \cdot \mathbf{r}) \right|^2 \\
= \sum_{j, k, G} n^j(k) |C_{G,j}(k)|^2 \delta(\mathbf{p} - \mathbf{k} - \mathbf{G}), \tag{1}
\]

where \( \psi_{k,j}(\mathbf{r}) \) and \( \psi_{+,\mathbf{p}}(\mathbf{r}) \) are the electron and positron wave functions, respectively, \( n^j(k) \) is the electron occupation density in \( k \)-space in the \( j \)th band, \( \mathbf{G} \) is a reciprocal lattice vector, and \( \gamma(\mathbf{r}) \) is the so-called enhancement factor which takes account of electron–positron correlations (and would be unity in the independent particle model (IPM)) [48]. The \( C_{G,j}(k) \) are the Fourier coefficients of the interacting electron–positron wave function product and the \( \delta \) function expresses the conservation of crystal momentum. \( \rho^{2\nu}(\mathbf{p}) \) contains information about the occupied electron states and their momentum, \( \mathbf{p} = \hbar(\mathbf{k} + \mathbf{G}) \), and the FS is reflected in the discontinuity in this occupancy at the Fermi momentum, \( \mathbf{p}_F = \hbar(\mathbf{k}_F + \mathbf{G}) \). The quantity \( n^j(k) \), which is of primary interest if one wants to know the occupied regions of the Brillouin zone and hence the shape of the FS, can be obtained by the so-called Lock-Crisp-West (LCW) folding [49] in which the FS signatures (which have been dispersed over (real) momentum space by the \( \delta \) function in (1)) are brought back into the first Brillouin zone.

2.2. Experimental details

In the centre-of-mass frame of the annihilating electron–positron pair, the two \( \gamma \) photons must be emitted in exactly opposite directions, each carrying away half of the energy of the system. However, in the laboratory frame, the two photons will generally not be anti-parallel and there will be some angular deviation between them, reflecting the momentum of the pair (in the laboratory frame) immediately prior to annihilation. At zero temperature, the momentum of the thermalized positron is negligible, and is therefore ignored in the derivation.

In the laboratory frame, let the two \( \gamma \)-photons have momenta \( \mathbf{p}_1 \) and \( \mathbf{p}_2 \), and energies \( E_1 \) and \( E_2 \) respectively, forming angles \( \phi/2 \) and \( \theta/2 \) with respect to the \( x-z \) and \( y-z \) planes.
Figure 1. Schematic of the $2\gamma$ annihilation observed in a 2D-ACAR measurement. The angles between the $\gamma$ rays are indicated as $\theta$ and $\phi$.

Resolving the total momentum along three orthogonal directions, $\hat{x}$, $\hat{y}$ and $\hat{z}$, we obtain,

$$
p_x = (|p_1| + |p_2|) \sin(\theta/2) \cos(\phi/2),
$$

$$
p_y = (|p_1| + |p_2|) \sin(\phi/2),\tag{2}
$$

$$
p_z = (|p_1| - |p_2|) \cos(\theta/2) \cos(\phi/2).
$$

Energy conservation requires that

$$
E_1 + E_2 = 2m_e c^2,\tag{3}
$$

where $m_e$ is the electron rest mass, and $c$ is the speed of light. Note that the binding energy of the electron–positron pair is too small to be included. In terms of the momenta of the $\gamma$’s, equation (3) can be written,

$$
c(|p_1| + |p_2|) = E_1 + E_2.\tag{4}
$$

Thus substituting (4) into the expressions for $p_x$ and $p_y$ in (3) generates,

$$
p_x = 2m_e c \sin(\theta/2) \cos(\phi/2),
$$

$$
p_y = 2m_e c \sin(\phi/2).\tag{5}
$$

A simple calculation reveals that an electron with a typical Fermi momentum will only contribute $\sim 10^{-3} m_e c$ to the total pair momentum, and since $|p| <\ll 2m_e c$, equations (5) (in the small angle approximation) become,

$$
p_x \approx mc\theta,
$$

$$
p_y \approx mc\phi.\tag{6}
$$

Thus (6) express the equivalence between the angular distribution $N(\theta, \phi)$ of annihilation $\gamma$’s and the distribution of the $x$ and $y$-components of the momentum of the annihilating electron–positron pair.
electron–positron pair, \( N(p_x, p_y) \). A 2D-ACAR experiment measures a 2D projection (or integral), \( N(p_x, p_y) \), of \( \rho^{2\gamma} \),

\[
N(p_x, p_y) = \int_{-\infty}^{\infty} \rho^{2\gamma}(p) dp_z.
\]

2.3. Reconstruction

Judicious choice of projection direction can, in certain circumstances, reveal the FS directly [50]. Generally the superposition of FS features in \( \rho^{2\gamma} \), due to the once-integrated nature of the projections measured in 2D-ACAR, could be considered a limitation of the positron technique. It is true that projections can sometimes be difficult to interpret, particularly by those who may be accustomed to viewing cross-sections through the FS. The efficient communication of results and comparison with theoretical predictions are certainly hindered by the projection process. To be able to produce a fully 3D \( \rho^{2\gamma} \) is therefore highly desirable.

The development of techniques for reconstructing a 3D density from its linear projections owes its rapid growth to Hounsfield’s invention of the x-ray computer assisted tomography (CAT) scanner [51] as a diagnostic tool. A plethora of reconstruction algorithms now exist in the field, keeping pace with the rapid advancement in computer processing power, some of which have also found application outside medicine. It is the requirement of reconstructing from a small number of projections (\( \leq 6 \)) that forces one to abandon algorithms optimized for medical reconstruction (where hundreds of projections are measured).

A scheme suggested by Cormack, the other pioneer of CAT who focussed on the mathematical basis of reconstruction [52, 53], was, however, applied to 2D-ACAR data by Kontrym-Sznajd [54]. It involves reconstruction on particular planes whose normals lie perpendicular to the projections’ integration directions. Originally proposed for medical application, the approach is of great utility in the 2D-ACAR field primarily because of the smooth nature of the densities to be reconstructed.

In addition to the benefits detailed in Kontrym-Sznajd’s original paper [54], our practical experience of using Cormack’s method for FS measurement has shown one further great advantage over Fourier-transform based methods connected with those methods introducing strong oscillations into the reconstructed densities at low momentum. For examples of these low momentum artefacts, coming from the final inverse Fourier transform, see [55, 56]. It is also worth noting the recent attempts to avoid this problem by explicitly removing the contribution from the first Brillouin zone in the data analysis [57]. An early review of reconstruction algorithms can be found in [55] and a more recent summary can be found in [58, 59]. Cormack’s method has been applied by us in a wide range of materials and to momentum densities coming not only from positron annihilation but also x-ray Compton scattering [40, 41, 44, 47, 60]. Fretwell et al [56] combined the Maximum Entropy deconvolution with tomography to show that the resulting reconstructions were superior to ones obtained from unprocessed data; the data presented here have undergone such a process.

Once the full 3D TPMD has been reconstructed, to directly visualize the FS it is necessary to fold the experimental \( p \)-space (real momentum) data back to \( k \)-space (crystal momentum) by applying the LCW folding procedure as described earlier [49]. Within this so-called reduced momentum density (RMD) the FS sheets may be identified by discontinuities. By looking for peaks in the magnitude of the directional derivative of the RMD the \textit{loci} of these discontinuities
may be identified. Furthermore, it has been shown [37] that the modulating effects of the positron wavefunction do not shift the location of the peaks in the directional derivative.

3. Electronic structure calculations on Ni$_2$MnGa

Interpreting and understanding the data produced in a 2D-ACAR experiment can be greatly assisted by the use of complementary electronic structure calculation. The calculations presented here were performed with our in-house linearized muffin-tin orbital (LMTO) code, within the atomic sphere approximation (ASA) with combined correction terms [61]. The electronic structure of Ni$_2$MnGa was converged within the cubic Heusler structure with an experimental lattice constant of $a = 5.82$ Å on 505 $k$-points within the irreducible Brillouin zone. Our bandstructure for the fully spin-polarized state was found to be in excellent agreement with previous studies [20, 22]. Spin-polarized Ni$_2$MnGa has 5 sheets crossing the Fermi level; the 17th, 18th and 19th bands in the majority channel, and the 13th and 14th bands in the minority channel (see figure 2 for examples of these FS sheets; our FS is in excellent agreement with that presented by [28]). Our free moment calculations (in which there are no constraints on the total moment) found the saturation spin moment to be 3.97 $\mu_B$, the majority of which (3.13 $\mu_B$) is on the Mn atom. This is slightly less than previous studies [20] and the experimental moment, both of which are close to 4.1 $\mu_B$. This slight discrepancy is likely to be caused by the partitioning of space within the ASA, compared to other full potential methods. A magnetic Compton scattering experiment, backed up by fully relativistic calculations, found only a negligible orbital moment, $\sim 1\%$ of the total [62]. The magnitude of the band splitting has a profound effect on the nesting properties of the FS; this is the subject of the next section.

3.1. FS Nesting in Ni$_2$MnGa

In order to address the question of whether Fermi surface nesting could lead to the lattice instabilities in Ni$_2$MnGa it is necessary to calculate the generalized susceptibility, $\chi(q, \omega)$, defined as:

$$
\chi_0(q, \omega) = \sum_{n,m,\omega,k} \frac{f(\epsilon_{n,k}) - f(\epsilon_{m,k+q})}{\epsilon_{n,k} - \epsilon_{m,k+q} - \hbar \omega - i\delta},
$$

where $f(\epsilon_{n,k})$ is the fermi function, $\omega$ is the frequency and $\epsilon_{n,k}/\epsilon_{m,k+q}$ is the state scattered from/to.

By looking at the magnetization as a function of temperature, Lee et al [19] were able to track how the nesting features of the 17th majority sheet evolved, and identified that it nested at approximately the correct vector at the PM transition temperature. By fixing the spin moment to reduced values we also were able to investigate finite temperature effects on the nesting features of the FS. We take 100% spin-polarization to be the saturation experimental moment (4.17 $\mu_B$ [1]). The evolution of the 17th majority sheet, and 14th minority sheet as a function of temperature (with the effect this has on the proposed nesting features highlighted) is shown in figures 2(b) and (d).

The effect that the changes in the shapes of these sheets has on the value of $\chi_0(q, \omega)$ is plotted in figure 3. Our results for the 17th majority sheet alone show a strong peak at the PM transition temperature, in excellent agreement with Lee et al [19]. Furthermore as the simulated temperature approaches that of the M transition ($T_M$ is expected to occur at
Figure 2. Spin-polarized FS of Ni$_2$MnGa, showing the (a) 17th majority hole sheet and (c) both the 13th (green) minority hole sheet and the 14th (red) minority electron sheet. Cuts through the FS at $k_z = \pi/a$ and $k_z = 2\pi/a$ of the 17th majority sheet and 14th minority sheet, respectively, are shown in (b) and (d). The cuts through these FS sheets plot their evolution as a function of spin moment, with the proposed nesting vectors indicated with arrows.

\[ \text{\sim} 93\% \text{ of the saturated moment) the peaks in the susceptibility due to the 17th majority band, and the 14th minority band converge to a vector very close to 0.43, the wavevector of the modulations in the 5M phase [6, 10]. Increasing the splitting of the bands causes the 17th majority sheet to shrink, and the 14th minority sheet to grow, causing the previously disparate nesting features to converge to the same value (see figure 2). The effect of this convergence on the total susceptibility is to cause the peak to sharpen as shown in the inset to figure 3, motivating the view that FS nesting may play a role in the modulations in the M phase as well as the PM phase. It is noteworthy that here we have just considered the intra-band nesting of these sheets; this is expected to minimize the effects of the neglect of matrix elements in the calculation of $\chi_0(q, \omega)$ [63]. Furthermore the peaks which we have identified in the real part of the susceptibility have their origins in the imaginary part, confirming that they are related to the nesting properties of the FS.

3.2. Computing the two-photon momentum density

To compare the predictions from our calculations with the 2D-ACAR data it is necessary to compute a theoretical equivalent to that measured in a 2D-ACAR experiment, viz the TPMD
Figure 3. Real part of the generalized susceptibility for the (a) 17th majority sheet and (b) the 14th minority sheet, with a \( \mathbf{q} \) vector along the [110] crystallographic direction. The inset displays the real part of the total \( \chi_0(\mathbf{q}, \omega) \) for the highest spin moment calculations; this quantity is summed over all bands.

(see (7)). Our code accomplishes this by expanding the muffin-tin orbitals on which the ground state is converged onto plane waves, which are then Fourier transformed to momentum space [61]. Key to interpreting 2D-ACAR data is a correct description of the enhancement due to the positron wavefunction. Recently it has been shown that an excellent description of the positron can be obtained when a state-dependent enhancement is considered [37]. It is possible to resolve the enhancement factor \( \gamma(\mathbf{r}) \), given in (1), onto \( \gamma_{n,l} \) which is explicitly independent of \( \mathbf{r} \) and \( \mathbf{k} \), but depends only on atomic species \( n \) and orbital angular momentum number \( l = s, p, d, f \). As before, within the IPM each \( \gamma_{n,l} \) is equal to unity. Whilst explicit momentum and position dependence is missing from this description of the enhancement, they are included implicitly due to the strong variations in band character through both real and reciprocal space; for more detail see [37]. This state-dependent enhancement of the positron is determined empirically; the agreement between the calculated RMD and that measured is iteratively maximized using the MINUIT package [64], with \( \gamma_{n,l} \) as a free parameter.
4. Two-dimensional angular correlation of positron annihilation radiation measurement of \( \text{Ni}_2\text{MnGa} \)

The sample used for this investigation was a large single-crystal grown using the Bridgman method. In order to minimize the concentration of vacancy defects which could trap the positrons the sample was annealed at 500K for two weeks. Our sample exhibits a \( T_C \) at 350 K, a \( T_{PM} \) at 220 K and a \( T_M \) at \( \sim200 \) K. The magnetic moment is sensitive to the sample stoichiometry [65], and these temperatures are largely consistent with those expected for stoichiometric \( \text{Ni}_2\text{MnGa} \) [65], although the enhanced \( T_C \) suggests a slight Ni excess in place of Mn.

The 2D-ACAR measurements were performed using the Bristol Anger Camera spectrometer. Six 2D-ACAR spectra of \( \text{Ni}_2\text{MnGa} \) were measured in the ferromagnetic phase, at \( T = 300 \) K under a magnetic field of \( \sim0.7 \) T applied parallel to \( \langle 100 \rangle \). The magnetic field is required to focus the positrons emitted from a \( ^{22}\text{Na} \) source onto the sample. At this field and temperature our sample is expected to exhibit a moment of \( \sim75\% \) of the saturation value [24]. The 2D-ACAR projections were equally spaced between the \[100\] and \[110\] crystallographic directions for the purposes of effective tomographic reconstruction. Each projection contained of the order of \( \sim200 \) million raw counts; the FWHM of the momentum resolution at this temperature corresponded to \( \sim17\% \) of the Brillouin zone. The raw profiles were deconvoluted using the Maximum Entropy procedure [38] prior to the tomographic reconstruction of the 3D momentum density.

The 2D-ACAR RMD measurements for the \[100\] and \[110\] directions are shown in figure 4, in which they have been folded back into the first Brillouin zone. The densities predicted by our LMTO calculations are also shown in figure 4. The top left of each panel shows the density predicted from a raw LMTO prediction within the IPM for a fully...
Table 1. Details of the $\chi^2$ test taken between theoretical TPMD projections and the experimental 2D-ACAR data. The improvement in the $\chi^2$, caused both by reducing the spin moment and allowing the state-dependent enhancement of the positron to be fitted, is clear. Underneath the details of the fitted enhancements for the different atomic sites and electron characters are shown, with $\gamma_p$ normalized to unity.

| IPM $\chi^2$ | SD $\chi^2$ |
|---------------|--------------|
| Moment        | [100] | [110] | Total | [100] | [110] | Total |
| 100%          | 1.78   | 1.90   | 1.84   | 1.18   | 1.31   | 1.24   |
| 85%           | 1.69   | 1.81   | 1.75   | 1.10   | 1.24   | 1.17   |

State-dependent enhancement

| Atom | Enhancement | Character | Enhancement |
|------|-------------|-----------|-------------|
| Ni   | 0.23        | $\gamma_s$ | 1.92        |
| Mn   | 0.18        | $\gamma_p$ | 1.00        |
| Ga   | 0.35        | $\gamma_d$ | 0.60        |
|      |             | $\gamma_f$ | 0.72        |

spin-polarized calculation, whereas the bottom left panel takes into account both the reduced spin moment expected under the experimental conditions, and the effects of positron enhancement.

In previous studies [36, 39] it has been possible to maximize the agreement between data and theory by empirically fine-tuning the calculated band structure by allowing small rigid shifts in energy. In this case, however, it was found that the statistical precision of the data was insufficient to resolve the complex multi-band spin-split semi-degenerate FS sheets. We were, however, able to fit the state-dependence of the positron enhancement, finding typical results expected for transition metals; the derived enhancements are shown in table 1. The positron was found to preferentially annihilate with electron states of $s$ character, as expected from their delocalized nature and thus large overlap with the positron wavefunction (which is strongly repelled by the atomic nuclei). Similar arguments follow for the observed de-enhancement of the $d$ electron states, as these are, of course, the most localized. The $f$ enhancement was included in the fit for completeness, but is not physically meaningful since these states are above $E_F$. The atomic site enhancements were determined using the Jarlborg–Singh local density approach to electron–positron correlation [48]; these were found to be consistent with the data. The positron preferentially annihilates on the Ga site, followed by the Ni sites with the Mn site being sampled least. This is consistent with the positron affinities for these elements [66].

We also found that by reducing the spin moment of the calculation the agreement was improved further, supporting the conclusion that at the temperature and magnetic field of the measurements, the moment of the sample was not fully saturated. A reduction to $\sim 85\%$ of the saturation moment was found to be consistent with the data. Returning to figure 4, the improvement from correctly accounting for the effects of the positron can be seen in the description of the TPMD (a) along WX–ΓX, and (b) along ΓK–L, as well as the shape of the high density at the X point. The degree of this improvement is quantified in table 1,
Figure 5. Cut through the Brillouin zone at $k_z = \pi/a$, the left half of the plot showing the calculated LMTO momentum density for the reduced moment calculation (broadened with a Fermi function) and the right half showing the experimental data. Overplotted are contours of constant occupancy, as determined from the calculated FS breaks for the reduced moment calculation.

wherein the $\chi^2$ for the fitted calculation is reduced to $\sim 60\%$ of its original value. Out of the six directions measured we have displayed the [100] and [110] directions only; owing to their higher symmetry they contain much more structure than the other directions and therefore dominate in the fitting procedure.

The full 3D momentum density is then obtained by applying the Cormack tomographic procedure, as explained earlier, to the six measured 2D-ACAR projections. The data were first deconvoluted using the MaxEnt procedure $[38, 56]$. A cut through the Brillouin zone at $k_z = \pi/a$ of the reconstructed momentum density is shown in figure 5. Also displayed in this figure is the momentum density as predicted from LMTO calculation (including the state-dependent enhancement due to the positron). As can be seen the agreement is generally very good, but there are some significant differences. The low densities predicted at the $L$ points are more prominent in the theory than the data, and are due to the 13th minority sheet (shown in figure 2). The square area of low density due to the 17th majority sheet, predicted at the centre of the cut also appears washed out in the data although hints of its presence remain. These discrepancies could be due to the small extra broadening introduced by the reconstruction process, or they could indicate non-Stoner like reductions in the band splitting which are not described by our calculations.

Further to this, by identifying discontinuities in the directional derivative of this quantity it was possible to extract 3D FS contours from the data; these are shown in figure 6. This
Figure 6. (a) and (b) show isosurfaces of the 3D tomographic reconstructions of 2D-ACAR data, determined from discontinuities in the 3D momentum density. (c) and (d) display the expected contours from the TPMD for the reduced moment calculation, which were extracted in the same way as the experimental contours and includes the expected Fermi broadening. An animation of this figure (movie 1) is available at stacks.iop.org/NJP/14/035020/mmedia.

provides an alternative and complementary method for analysing the experimental data. As before the predictions from calculation are displayed alongside the experimental data. In this case the theoretical FS sheets were extracted in an analogous way to the data, i.e. by calculating the 3D momentum density, and then by identifying discontinuities in its directional derivative. Referring back to the calculated FS sheets shown in figure 2, the 14th minority sheet is clearly present in our experimental data. Interestingly it is also possible to resolve the nesting features identified in figure 2(d). The nesting vector for our reconstructed FS sheet is at \( \mathbf{q} = [0.47, 0.47, 0] (2\pi/a) \), which is consistent with the theoretical scenario for a reduced moment state, and is close to the 5M modulating wavevector below \( T_M \) [6, 10]. The situation for the 17th majority sheet (also identified in figure 2) is less clear. The sheet extracted from the experimental density (figure 6(a)) is in good agreement with that extracted from the calculation (figure 6(c)). However, the proposed nesting features are obscured by the presence of the 13th minority sheet, which crosses the 17th majority sheet along \( \Gamma - L \). While it is not possible to directly resolve the nesting features, figures 5 and 6 find the 17th majority sheet to be in excellent agreement with LMTO calculation. This still lends weight to the arguments from electronic structure calculations [19] that this sheet is strongly nested at the same wave vector as the experimentally observed phonon softening prior to the PM transition [7]. As can also be discerned from figure 5.
(by the shape of the experimental RMD along W–L–W), the width of the 13th majority FS sheet appears considerably smaller in the data than the LMTO prediction. The other two FS sheets (the 18th and 19th majority sheets) are not separable from the contour displayed in figure 2(b), due to their near-degeneracy with the 14th minority electron sheet. Generally our data are found to be in very good agreement with LMTO calculation. The small discrepancies observed could be ascribed to subtle non Stoner-like effects on the band splitting.

It is well known that the MT does not require FS nesting, and is usually ultimately driven by the band Jahn–Teller effect. As mentioned earlier, a recent study on Co$_2$NiGa by Siewert et al [15] has identified an MT in a compound, which exhibits neither FS nesting nor a band Jahn–Teller effect. They point to disorder and strong electron–phonon coupling as the cause of the MT. There are two factors dictating the role that electrons play in lattice instabilities, namely electron–phonon coupling and FS nesting. Siewert et al argue that whilst the second factor is missing from Co$_2$NiGa, strong electron–phonon coupling could still lead to the instability. Returning to Ni$_2$MnGa, here we have confirmed the presence of a strongly nested FS, and one which nests at the modulating vector observed in the Martensitic phase of this compound. FS nesting is only part of the process which leads electrons to destabilize the lattice, but it is able to greatly enhance the effects of electron–phonon coupling for particular wavevectors. In this compound it seems likely that it plays an important role in determining the atomic modulations associated with the various Martensitic phenomena.

5. Conclusion

We have presented a positron annihilation measurement of the electron momentum density within Ni$_2$MnGa, alongside complementary electronic structure calculations. We find the measurements to be in excellent agreement with the predictions from electronic structure calculation. Furthermore we were able to extract experimental FS contours from this momentum density, and have observed the nesting features which have been previously identified in theoretical calculations of the FS of this alloy, and are believed to influence the modulations adopted in its low temperature Martensitic phase. These results suggest that it may be possible to extend this analysis into other parts of the phase diagram of Ni$_{2+x}$Mn$_{1-x}$Ga, to observe how the FS changes with stoichiometry, and it may also be possible to measure below T$_{M}$. These measurements may introduce considerable technical difficulties, as defects introduced by doping or the Martensitic transition may trap the positrons, precluding the formation of the Bloch states required for a Fermi surface measurement.

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