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Temperature Dependence of Spin Density in Ni$_3$Al: Comparison with Pure Ni

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PACS.75.25.+z – Spin arrangements in magnetically ordered materials (including neutron and spin-polarized electron studies, synchrotron x-ray scattering, etc.)

Abstract. — The results of a spin density measurement in the compound Ni$_3$Al as function of both temperature and magnetic field are reported. A comparative analysis of the present data with those measured in both Ni$_3$Al at 4.2 K (Felcher G.P. et al., Phys. Rev. B16 (1977) 2124) and pure Ni at various temperatures (Brown P.J. et al., J. Phys. I France 1 (1991) 1529) is presented. By means of this analysis, the deformation of the electron distribution is deduced and the connection with the formation of a magnetic phase in Ni-based systems is enhanced.

1. Introduction

In the last forty years there has been a great deal of measurements on the spin density distribution in ferromagnetic transition metals and alloys by means of polarized neutron diffraction. Such a technique has been proved to be a very powerful tool to measure the magnetic moment distribution at atomic scale. Most part of the investigations performed to date were carried out at temperatures rather low in comparison with the Curie temperature, hence most part of the available body of data is representative of the zero-temperature behaviour of these systems. Only a limited set of experimental data is available at temperatures which represent a sizeable fraction of the Curie temperature.

A satisfactory theoretical description of the zero-temperature properties of transition metals is provided by the Density Functional approach within the framework of the Local Spin Density Approximation (LSDA) [1]. Moreover, there are considerable advances in first principle theories [2–4] for the description of the finite temperature behaviour of these systems, even though fewer experimental data are available and the theory has been developed at a lower degree of accuracy. Failures of the LSDA in calculating the zero-temperature spin density in transition metals and alloys have been discussed in reference [5].

Recently a detailed investigation of the temperature dependence of the spin density in Ni above room temperature has been published [6]. Although only a weak temperature dependence of the magnetic form factor was reported in reference [6], it is important to further

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investigate the behaviour of the spin density as a function of the temperature in Ni and Ni-based systems as a key to understand the mechanism giving rise to ferromagnetic alignment. Considering that the Curie temperature of Ni (628 K) [6] and those of the experiment performed in reference [6] (298 K-645 K) are comparable with the Debye temperature (~420 K), the presence of vibrational contributions affecting the data of such an experiment might be not negligible. A temperature dependence study of the spin density in the intermetallic compound FeCo was carried out [7] to mainly identify the effect of lattice vibrations on the electron distribution. In such a sample, the Curie temperature (~1450 K) is much higher than the Debye temperature (~450 K) and the major effect observed at the temperature of the experiment (1000 K) was ascribed to the fluctuation induced by the nuclear vibrations.

Therefore, the study of a Ni-based system with a very low Curie temperature, which were also relatively lower than the Debye temperature, would be extremely valuable to outline the behaviour of the spin density of Ni close to the Curie point. There are two possible simple choices, namely Ni-Cu alloys and the Ni$_7$Al compound. The first class of samples has the disadvantage that the magnetic behaviour of copper in the system is not well defined. On the other hand it is known that Al in Ni$_7$Al compound carries a negligible magnetic moment [8-10]. Therefore we decided to extend the spin density measurements performed in reference [8] on Ni$_7$Al at 4.2 K to temperatures close to the Curie point (~70 K). By a comparative analysis of the data in Ni$_7$Al compound and those already available in pure Ni, the relevant contributions to the spin density of Ni can be identified and the corresponding temperature dependence can be outlined.

The description of the temperature dependence of the spin density can, in turn, highlights some aspects of the ground state of the system. Due to exchange-correlation interaction, the magnetic state is favoured by the contraction of the $up$ spin electron density together with the expansion of the $down$ spin electron density. This behaviour makes the energy of the magnetic state lower than that of the non-magnetic state and it is well tailored by the negative spin density present in the interstitial regions of the unit cell [6]. The analysis of the magnetic state when reducing the magnetic moment should give information on the difference between $up$ and $down$ spin electron densities and hence on this basic mechanism which should make the magnetic state energetically favoured.

2. Experiment and Data Reduction

The sample of the present experiment was carefully chosen to match the same magnetic properties as that investigated in reference [8]. The magnetic properties of the compound Ni$_7$Al are known to be strongly dependent on the Al content [11], so that data collected in different samples can be compared only when the compositions are very close to each other. The composition of the present sample was deduced by measuring the Curie temperature and the lattice parameter by X-ray diffraction ($a_0 = 3.558 \pm 0.002$ Å). From these measurements a consistent result was obtained, namely the Ni content was found to be 76.3 ± 0.1%. This composition corresponds to a Curie transition temperature $T_C = 77$ K and it is close enough to the composition reported in reference [8] (75.9%) in order that the magnetic form factors are comparable.

The experiment was performed on the polarized neutron diffractometer installed at the 1-MW Training, Research, and Isotope Production Reactor of the Centro Ricerche Energia-Casaccia (Rome). The experimental setup was that standard in this kind of measurements. A Co$_92$Fe$_8$ monochromator was employed to produce a polarized and monochromatic neutron beam, the neutron spin flipper was operated at 3 Hz frequency, a vertical magnetic field was applied to the sample and the diffracted beam was detected in the horizontal plane.
The sample was in the shape of a vertical slab having dimensions $1 \times 7 \times 20 \text{ mm}^3$ with the extended face parallel to the (100) plane and the long axis perpendicular to the (011) plane. The crystallographic structure of the stoichiometric compound Ni$_3$Al is the L1$_2$ type, based on a cubic fcc cell with two sets of non-equivalent crystallographic sites, namely corners (A-sites) and faces (B-sites). In the ideally ordered system, corners are occupied by Al and faces by Ni. The nuclear structure factor of superlattice reflections is given by:

$$F_S^{S}(hkl) = b_A - b_B$$

where $b_l$ is the total scattering amplitude of the $l$-th site. A measure of the state of order of the sample is given by the long-range order parameter $S$ which is defined as:

$$S = \frac{F_S}{b_{AI} - b_{NI}}$$

and $F_S$ is the measured structure factor of the superlattice reflections. The state of order of the present non-stoichiometric sample was checked by measuring the integrated intensity of the three reflections (100), (200) and (400) at room temperature. The experimental value $|F_S| = 0.68 \pm 0.02 \times 10^{-12} \text{ cm}$ was obtained for the superlattice nuclear structure factor. Such a value compares quite well with that calculated assuming a full occupancy of the Ni-sites by Ni atoms and Ni atoms in excess located at the Al-sites, i.e. $0.658 \times 10^{-12} \text{ cm}$. The distribution assumed for the Ni excess is as in reference [8]. The flipping ratios of the four innermost fundamental reflections and the first superlattice reflection were measured as a function of temperature and magnetic field in the ranges 30 K-80 K and 0.01 T-0.73 T. The incoming neutron wavelength was $\lambda = 0.89 \text{ Å}$. The sample was cooled down by using a closed-cycle refrigerator whose cold finger was inserted in the gap of the electromagnet providing the magnetic field. The temperature was continuously monitored by means of a Pt resistor and it was stable within 0.5 K. The intensity of the magnetic field at the sample was measured by means of a Hall-effect gaussmeter. Standard corrections for incomplete polarization of the incoming beam, flipping efficiency and half-wavelength contamination were applied to the measured data. The amount of extinction was determined by measuring the flipping ratios of (111), (220) and (222) reflections at 33 K and 0.73 T at two different wavelengths, namely 0.89 Å and 1.26 Å. The extinction correction for the (111) reflection at 0.89 Å was found to be 13%, while smaller corrections had to be applied to the higher order reflections. The bulk magnetization of the sample was measured with a 0.73 T applied field by means of a ballistic magnetometer. The values of the bulk magnetic moment per unit cell were found to be $0.340 \pm 0.010 \mu_B$, $0.315 \pm 0.010 \mu_B$ and $0.231 \pm 0.010 \mu_B$ at 33 K, 40 K and 60 K respectively.

3. Data Analysis and Discussion

The present experimental data together with those reported in reference [8] were used to deduce the magnetic structure factors $F_M(G)$, where $G$ is a reciprocal lattice vector, using the tabulated values for the nuclear scattering amplitudes of Ni and Al, i.e. $b_{NI} = 1.03 \times 10^{-12} \text{ cm}$ and $b_{AI} = 0.345 \times 10^{-12} \text{ cm}$, properly weighted for the sample composition. The ratio $\gamma$ between magnetic and nuclear scattering amplitudes obtained from the present measurements on the (111) reflection as function of the magnetic field at various temperatures is shown in Figure 1. By increasing the magnetic field at the sample, a full saturation is reached both at 33 K and 40 K applied temperature, while at 60 K the $\gamma$-ratio is still increasing at 0.7 T. At 80 K the sample has a paramagnetic behaviour and its magnetization is essentially induced by the external field. The behaviour observed for the (111) reflection was recovered also.
for the other reflections. Therefore the data selected for the following analysis were those collected with the maximum applied field together with those measured in reference [8] at 1 T and 4.2 K. Making use of the bulk magnetization curve at 0.7 T as a function of the temperature, the magnetic form factors of the four fundamental reflections were deduced. The form factors $f(G) = F_M(G)/\mu$, $\mu$ being the bulk magnetic moment per unit cell, show a temperature dependence. From these data very little can be inferred about the mechanism which dominates the temperature dependence of the magnetic moment distribution around the Ni atoms, although a clear contraction of the form factor of the two innermost reflections is observed increasing the temperature. Because of the very low temperature range, as compared with the Debye temperature, the observed contraction actually concerns the magnetic form factor, lattice vibrations effects being definitely negligible. To get more information about this contraction of the form factor, a careful comparison with pure Ni should be performed. To this purpose a more detailed analysis of both the data of reference [8] on Ni$_3$Al and those of reference [6] on pure Ni was carried out. Considering that the Debye temperature and the Curie temperature are very close in pure Ni, possible effects due to lattice vibrations must be accounted for. By making use of the results obtained in FeCo [7], an approximate calculation of the deformation induced by lattice vibrations on the magnetic form factor in the temperature range of the measurements of reference [6] was carried out. By using the Debye-Waller factor, also measured in reference [6], the absolute change of the magnetic form factor induced by lattice vibrations was found not to exceed 0.03. Therefore, such an effect was completely neglected in the following analysis. The data collected in pure Ni [6] at room temperature, 500 K, 610 K and 645 K with a 4.6 T applied magnetic field were used to determine the spherical form factor through a direct integration of the magnetization over the Wigner-Seitz
cell, that is:

\[ f_{\text{sph}}(Q) = \frac{1}{\Omega_0 \mu} \sum_G F_M(G) \int_{\Omega_{\text{WS}}} \exp^{iG \cdot r} j_0(Qr) \, dr \]  

(1)

where \( \Omega_0 \) and \( \Omega_{\text{WS}} \) are the unit cell and the Wigner-Seitz cell volumes respectively and \( j_0(x) \) is the zero-th order spherical Bessel function. The integral over the Wigner-Seitz cell was calculated numerically using 4096 points uniformly distributed over the irreducible wedge. In this way the value of the integral is accurate to the third decimal place. Once the integral is performed the spherical form factor can be readily obtained. Use of the spherical form factor is made in the following analysis as a key quantity to describe the general trend of the spin density. However, since the measured structure factors contribute to equation (1) with different weights, \( f_{\text{sph}}(Q) \) has to be regarded as a derived quantity and not a direct experimental result. Moreover, \( f_{\text{sph}}(Q) \), as obtained from equation (1), contains series termination errors. To evaluate the size of the termination errors, a model structure factor for Ni metal was simulated through:

\[ F_{\text{mod}}(G) = 0.6 \langle j_0(G) \rangle - 0.3A_{hkl} \langle j_4(G) \rangle \]  

(2)

where the numerical coefficients are standard values for spherical and aspherical magnetic moment of Ni and \( A_{hkl} \) is the direction-dependent factor appropriate for cubic symmetry and d-electrons. Such a decomposition, that is quite common [6,12], is used in the present case to produce the structure factor at selected values of the reciprocal lattice vectors, with the advantage of containing as spherical and aspherical contributions, \( \langle j_0(G) \rangle \) and \( \langle j_4(G) \rangle \), the free ion calculated terms [13] which are continuous functions of \( Q \). The model structure factors \( F_{\text{mod}}(G) \) are then inserted into equation (1) to calculate the spherical form factor which can be directly compared with the nominally exact term \( \langle j_0(G) \rangle \). The two curves were found to agree within 0.007 over the \( \sin (\vartheta)/\lambda \) range from 0 to 0.7 Å\(^{-1}\). Therefore, the analysis procedure based on equation (1) was considered adequate for the present purposes. Nevertheless, some care must be taken in handling the spherical form factor \( f_{\text{sph}}(Q) \) since its behaviour in the low \( Q \) region is dominated by the structure factors of the first couple of reflections, that is an error on these measured structure factors can result in a systematic error in \( f_{\text{sph}}(Q) \) at low \( Q \).

A close inspection of the pure Ni form factors calculated from equation (1) shows a small, but well defined, temperature dependence which is almost linear when the form factor is plotted versus the bulk magnetic moment. In Figure 2 the experimental form factors \( f(G) \) of the first four innermost reflections, as measured in reference [6], are shown and a zero magnetic moment form factor can be easily extrapolated. Of course, the same behaviour is recovered for the spherical form factors obtained through equation (1). By means of the spherical form factors, an extensive extrapolation to zero magnetic moment can be carried out. The form factor obtained by this extrapolation procedure is shown in Figure 3 and, surprisingly, it is rather close to that of the free ion Ni\(^{2+}\) as calculated in reference [13]. This result suggests that the difference between the form factor of crystalline Ni at room temperature and the form factor of the free ion Ni\(^{2+}\) could be mainly due to the contribution of paired electrons and not to a true deformation of the electron density. In fact, the magnetic structure factor can be written as:

\[ F_M(Q) = n_\uparrow f_\uparrow(Q) - n_\downarrow f_\downarrow(Q) \]  

(3)
Fig. 2. — Experimental form factor of crystalline Ni [6] versus the bulk magnetic moment per atom. Results are shown for the first four reflections (111) (dots), (200) (circles), (220) (triangles) and (311) (squares). Error bars are of the same size as the symbols. The full curves are linear fits to the experimental data.

Fig. 3. — Spherical form factor of crystalline Ni obtained by linear extrapolation of the spherical form factors to zero magnetic moment (full line). Spherical form factor of the free ion Ni$^{+2}$ [13] (dashed line). Paired electron contribution to the form factor at 298 K (see text) for crystalline Ni (full line) and Ni$^{+2}$ (dashed line). The short-dashed line is the theoretical calculation of the paired electron contribution in crystalline Ni according to reference [15].

where $n^\uparrow$ ($n^\downarrow$) is the number of up (down) spin electrons and $f^\uparrow(Q)$ ($f^\downarrow(Q)$) is the up (down) spin form factor. The form factor is then given by:

$$f(Q) = \frac{F_M(Q)}{n^\uparrow - n^\downarrow} = \frac{1}{Z} [n^\uparrow f^\uparrow + n^\downarrow f^\downarrow] + 2 \frac{n^\uparrow n^\downarrow}{\mu_s Z} (f^\uparrow - f^\downarrow)$$

$$= f_0(Q) + f_{pair}(Q)$$

(4)

where $\mu_s = n^\uparrow - n^\downarrow$ is the spin magnetic moment and $Z$ is the total number of outer electrons. $f_{pair}(Q)$ is the contribution of the paired electrons that was first discussed by Hodges et al. [14]. This term arises from rather small differences between up and down spin form factors and it is enhanced by the relatively small denominator. The term $f_0(Q)$ represents the reference atomic form factor of the valence electrons and it is what is essentially derived when extrapolating the form factor to zero magnetic moment. It should be noted that the decomposition proposed in equation (4) is not the only possible one, although alternative forms give essentially the same structure. In Figure 3 the paired electron contribution, as deduced from the present analysis of Ni data at room temperature, is also shown. Since the Ni data span the $T/T_C$ range 0.47-1.01, low temperature data not being available, we found that in this range a linear extrapolation to zero magnetic moment of the form factor versus the magnetic moment gives essentially the same result as an extrapolation as a function of $1-T/T_C$. Of course a rather different situation occurs in the case of Ni$_3$Al where the data span the $T/T_C$ range 0.05-0.74.
Since an adequate set of data to derive the spherical form factor in Ni$_3$Al is not available, a properly suited analysis was carried out. The data of reference [8] were first used to deduce the spherical form factors of the Wigner-Seitz cells of both Ni and Al. This was done by use of equation (1) properly modified to treat a compound system [5]. To avoid convergence problems in the integral, the limited set of fundamental reflections from reference [8] was enlarged by adding the high order reflection data from pure Ni at room temperature properly scaled for magnetic moment and lattice parameter. It was found that even a 20% variation in the added data did not affect the magnetic moments and the spherical form factor in the $\sin \theta/\lambda$ range 0–0.5 Å$^{-1}$ we are going to examine. Considering that magnetic moments are very small in Ni$_3$Al, the Wigner-Seitz cell integrations were performed on a finer mesh consisting of 32768 uniformly spaced points in the irreducible wedge. By such a choice, accurate data could be derived at the Al-site where a very little magnetic moment is expected. The form factor at the Ni-site, which sensibly represents the form factor of the Ni atom in the compound (the Ni-site is occupied by Ni atoms only) is shown in Figure 4 in comparison with that of pure Ni at room temperature. As already observed in reference [8], the Ni form factor in Ni$_3$Al at 4.2 K is very close to that of pure Ni at room temperature.

It is interesting to note that the magnetic moment at the Ni-site is almost equal to the total magnetic moment of the compound. It was found $\mu_{\text{Ni}}^{\text{WS}} = 0.126 \mu_B$, while at the Al-site it was found $\mu_{\text{Al}}^{\text{WS}} = -0.007 \mu_B$. Considering that 3.6% of the Al-sites are occupied by Ni atoms, consequences are either that Ni atoms at Al-sites have a small negative magnetic moment or the Al-sites have a complex magnetic moment distribution whose integral over the Wigner-Seitz cell turns out to be negative. By use of these data only, no further information about the behaviour of the magnetic moment distribution at the Al-site can be inferred. The magnetic moments inside two equal touching spheres centered on the Ni and Al-sites were also calculated. The results were $\mu_{\text{Ni}}^{\text{sph}} = 0.124 \mu_B$ and $\mu_{\text{Al}}^{\text{sph}} = 0.014 \mu_B$. The comparison between these results with those obtained by integration over the Wigner-Seitz cell shows that there are regions where the spin density becomes negative with a sizeable magnetic moment within the sphere centered at the Al-site. The most reasonable interpretation of this result is that the excess of Ni present at the Al-sites carries a magnetic moment comparable to that of Ni at
the Ni-site. Since the probability of finding a Ni atom at the Al-site is 0.036 ± 0.004 [8], the magnetic moment of the off-site Ni atoms was calculated and found to be $\mu_{\text{Ni}}^{\text{eff}} = 0.38 ± 0.06\mu_B$, with the assumption of no-contribution from Al atoms. This value is slightly dependent on the sphere radius, so there is no reason in trying to interpret it by comparison with the magnetic moment of pure Ni. Tentatively one can say that the magnetic moment of the Ni atoms at the Al-site is larger than that at Ni-sites, probably as a consequence of the larger number of Ni atoms first-nearest neighbours. Further qualitative information can be gained by inspection of Fourier maps. The spin densities on (001) and (110) basal planes are shown in Figure 5. A well defined positive contribution is present at the Al-site, while a fluctuating and rather smooth spin density is present in the interstitial region. The negative spin density regions seem to be directly related to the Al-site, a small contribution being related to Ni atoms. The observed shape is again consistent with the following picture: the spin density at the Al-sites is dominated by the excess of Ni atoms located on these sites, whereas the negative magnetic moment found by integration over the Wigner-Seitz cell is due to the extended regions of negative spin density observed in the interstitial volume. As a final remark, the analysis of the Ni$_3$Al data at 4.2 K shows that, apart from the contribution of the Ni atoms at the Al-sites, the behaviour of the spin density strongly depends on the different shape of the up and down electron densities as in the case of pure Ni.

A rather sensible conclusion on the temperature dependence of the Ni form factor is obtained by studying the same dependence as observed in Ni$_3$Al. For such a sample the Curie temperature is so low as compared with the Debye temperature that any vibrational effect can be safely neglected. The experimental form factors of the four innermost fundamental reflections (111), (200), (220) and (311) measured at the highest magnetic field are shown in Figure 6 as a function of $1 - T/T_C$. The linear trend apparent from this figure shows that the temperature dependence of the magnetic form factor in Ni$_3$Al is similar to that observed in pure Ni. These findings allow to state that the decrease of the form factor of Ni with increasing the temperature is not related to atomic vibration effects. In Figure 6 the values of the extrapolated form factor $f_0(Q)$ from Figure 3 are also reported. A good agreement is found
Fig. 6. — Experimental form factors of Ni₃Al versus temperature for the first four fundamental reflections: (111) (dots), (200) (circles), (220) (triangles) and (311) (squares). The full squares are the \( f_0(Q) \) values as obtained in pure Ni (see text). Error bars are reported when exceeding the symbol size. The full lines are guide to the eye.

Table I. — Values of \( \mu f_1 \) for the Ni-site and Al-site in Ni₃Al at various temperatures. Data were obtained by comparing the magnetic structure factor of the (100) superlattice reflection with the value obtained extrapolating the fundamentals structure factor to the same \( \sin (\vec{q})/\lambda \) (see text).

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \mu_{\text{Ni}} f_{\text{Ni}} )</th>
<th>( \mu_{\text{Al}} f_{\text{Al}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>0.113 ± 0.002</td>
<td>0.000 ± 0.003</td>
</tr>
<tr>
<td>33</td>
<td>0.096 ± 0.002</td>
<td>0.012 ± 0.003</td>
</tr>
<tr>
<td>40</td>
<td>0.086 ± 0.002</td>
<td>0.011 ± 0.003</td>
</tr>
<tr>
<td>60</td>
<td>0.074 ± 0.002</td>
<td>0.014 ± 0.003</td>
</tr>
</tbody>
</table>

between the \( f_0(Q) \) values and the extrapolation to \( T_C \) of the Ni₃Al data. Therefore, \( f_0(Q) \) and \( f_{\text{pair}}(Q) \) turn out to be a characteristic of Ni atoms in both pure Ni and Ni₃Al compound and the discussion about the spin density around the Ni site appears to be well supported by the whole set of data. Finally, the structure factor of the (100) superlattice reflection can be used to determine the magnetic moments at Ni and Al-sites by comparison with that obtained extrapolating the structure factor of the fundamental reflections to the same value of \( \sin (\vec{q})/\lambda \), namely 0.141 Å⁻¹ The extrapolated value was obtained by using a simple polynomial fit to the structure factor of the fundamental reflections. By this procedure, only a minor error is introduced because of the small value of \( \sin \vec{q}/\lambda \) where the extrapolation is performed, that is the extrapolated form factor is very close to one. The site magnetic moments thus obtained are reported in Table I. Inspection of this Table shows that as the temperature increases, the difference between up and down electron densities decreases and, as a consequence, the negative spin density present at low temperature in the interstitial regions (Fig. 5) disappears. This is observed as an increase of the magnetic moment at the Al-site since the magnetic moment of the excess of Ni atoms is no more obscured by the negative contribution produced by the surrounding Ni atoms located at the Ni-sites.
4. Conclusion

The results presented in the previous section allowed us to observe directly from the experimental data that the formation of a magnetic phase in Ni and Ni$_3$Al is related to a deformation of the electron distribution in comparison with the free atom. Such a deformation is different for up and down spin states. In particular, a well defined expansion of the density of the down spin states with respect to the up spin states is present, thus producing a negative spin density in the interstitial regions of the unit cell. This negative density, already observed in early experimental investigations of the spin density in 3d metals and alloys, reflects the relevance of the negative exchange energy, which becomes more negative on accumulating a larger number of electrons in a given (majority) spin state around each site. A detailed analysis of the temperature dependence of the magnetic structure factors, as measured in polarized neutron scattering experiments, has shown that the difference between the experimental magnetic form factor and that of the free ion is dominated by the enhancement of the difference between up and down electron densities. This is fairly evident in Figure 3 where the average up and down form factor in Ni is compared with that of the free (+2) ion. It is also interesting to compare the present results for pure Ni with those obtained in the LSDA calculation of reference [15] for what concerns the paired electron contribution. For internal consistency, the magnetic form factor was calculated by direct Fourier transformation of the up and down electron densities reported in reference [15]. Because of the muffin tin approximation of such a calculation, the form factor is given by the sum of two contributions: one from the spherical density contained within the muffin tin, the other from the constant density present in the interstitial regions. Both contributions can be easily determined by numerical integration. By comparing the so derived magnetic form factor with that of the paramagnetic free ion Ni$_{1+2}$, the paired electron contribution also shown in Figure 3 was obtained. The small difference between calculated and experimental $f_{\text{pair}}(Q)$ can be also attributed to the neglect of the orbital contribution in reference [15]. Including the approximate orbital contribution as calculated for the free (+2) ion [16] or for crystalline Ni [17], an almost perfect agreement is found.

Finally, considering that the same $f_0(Q)$ curves are obtained in both Ni and Ni$_3$Al, while the same form factor is found at the highest magnetic moment, one can state that the contraction of the up spin electron density, with respect to the down spin electron density, is essential to make the magnetic phase of these Ni-based systems energetically favoured. This qualitative result, which is implicitly contained in the theoretical calculations, is highlighted by the present analysis of the experimental data.

The findings of the present work suggest that $f_0(Q)$ is rather independent of the local environment, however such a guess should be confirmed by further studies of fcc Ni-based systems. The analysis of the behaviour of systems with up spin states not full, in contrast with the case of Ni which has a full up spin band, will be also essential to get some more insight into the effect we have been considering.

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