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Reanalysis of polarised neutron data on NiRu using projection operator formalism

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Abstract. Projection operator formalism has been applied to analyse magnetic structure amplitudes in $Ni_{1-x}Ru_x$ ($x = 0{\cdot}027, 0{\cdot}033$ and $0{\cdot}046$) alloys. This method is suitable for metals and alloys as it does not assume any free ion form factor. A new prescription has been discussed for the local site moment and diffuse moment in this frame work. The results of the present analysis are compared with those obtained using form factor analysis.

Keywords. Polarised neutron; form factor; projection operator; NiRu alloy.

1. Introduction

During the past two decades a number of measurements of the neutron magnetic form factors have been reported in ferromagnetic elements and dilute ferromagnetic alloys (Mook 1966; Dobrzynski *et al* 1970; Ito and Akimitsu 1974; Livet and Radhakrishna 1976). The original analysis of experimental form factors on Fe, Co and Ni (Shull and Yamada 1962; Moon 1964; Mook 1966) are based on a model in which the magnetisation density is described as a superposition of free-ion density localised at the atom site and a nearly uniform diffuse moment density. Under this assumption the form factor at any reciprocal lattice (κ) is given as (Mook 1966)

$$f(\kappa) = 2/g\,[(1+\alpha) f^s(\kappa) - \alpha\delta(\kappa)] + \frac{g-2}{g} f^L(\kappa) \tag{1}$$

$$f^s(\kappa) = \langle j_0 \rangle + A_{hkl}(5\gamma/2 - 1)$$

$$f^L(\kappa) = \langle j_0 \rangle + \langle j_2 \rangle$$

$$\langle j_n \rangle = \int [U(r)]^2 j_n(\kappa r)\,\mathrm{d}r$$

where $f^s(\kappa)$ and $f^L(\kappa)$ are the 'spin' and 'orbital' form factors. A_{hkl} is the geometrical factor. $U(r)/r$ is the radial part of the one electron wave function and $j_n(\kappa r)$ are spherical Bessel functions. The expression (1) is fitted to measured neutron form factors with the asphericity parameter (γ) and the fraction (α) of total spin moment that is present throughout the Wigner Seitz (ws) cell as free parameters, $\langle j_0 \rangle$ and $\langle j_4 \rangle$ were calculated using free ion $U(r)/r$.

This atomic model though highly successful for Fe, Co and Ni suffers from the following drawbacks: (i) In principle its application to metallic systems can be questioned as the magnetic electrons in metals are itinerant and do not preserve their

atomic character. (ii) The α value is sensitive to the choice of form factors. (iii) In alloys the assumption of atomic or ionic form factors for pure constituents is not correct as they may change on alloying. As a first modification to the atomic model, in the analysis of the data on $Ni_{1-x}Ru_x$ (Chakravarthy *et al* 1980 hereafter referred as I), the $\langle j_0 \rangle$ values were derived from the measured magnetic structure amplitudes (Moon 1971). However for $\langle j_2 \rangle$ and $\langle j_4 \rangle$ the calculated free ion values relative to the Ni^{2+} ion were used (Watson and Freeman 1961).

Recently a projection operator (PO) formalism has been reported to analyse the magnetic structure amplitudes in metals and alloys (Kaprzyk *et al* 1981). In this formalism the point group symmetry of the magnetic electrons has been exploited to get a set of projection operators in matrix form which can project out the measured form factors into the sphere inscribed within the ws cell. The projected form factors are then compared with the corresponding parts of form factors of the atomic sphere magnetisation.

Distinct advantages of this method over the earlier ones are: (i) no assumption is made for any part of the form factor, all being derived from the magnetic structure amplitudes. (ii) In alloys one deals with the site form factors without involving the form factors of individual constituents. (iii) Both the experimental and calculated form factors which are compared, correspond to the atomic sphere magnetisation. Application of this method to polarised neutron data on Fe and Ni shows that α is very small compared to those obtained using the traditional form factor analysis (Kaprzyk *et al* 1981). Further it has been shown that form factor analysis when made using form factors from the PO formalism and fitting it to the projected experimental form factors rather than the raw ones result in small α values (van Laar *et al* 1982). In view of the foregoing, we have sought to reanalyse our NiRu data using the PO formalism, as it has distinct advantages over the earlier method. The results are compared with those obtained in I.

2. Main feature of the PO formalism

A full description of the projection operator formalism is given by Kaprzyk *et al* (1981). Here we recapitulate some of its salient features.

The magnetisation density $M(\mathbf{r})$ at any point in the ws cell is given by

$$M(\mathbf{r}) = 1/V_0 \sum_{\kappa} M(\kappa) \exp(-i\kappa\cdot\mathbf{r}) \tag{2}$$

where $M(\kappa)$'s are the measured magnetic amplitudes and V_0 the unit cell volume.

For cubic symmetry (2) can be rewritten as:

$$M(\mathbf{r}) = 1/V_0 \sum_{\{\kappa\}} M(\kappa)\,\omega(\kappa)\,\mathrm{SPW}(\kappa, \mathbf{r}) \tag{3}$$

$\omega(\kappa)$ is the number of equivalent κ's of vector star $\{\kappa\}$ and SPW $(\kappa, \mathbf{r})$ are symmetrized plane waves.

Further, $M(\mathbf{r})$ can be expanded in terms of cubic harmonics $K_l(\hat{\mathbf{r}})$

$$M(\mathbf{r}) = \sum_l M_l^0(r)\, K_l(\hat{\mathbf{r}}) \tag{4}$$

where $M_l^0(r)$ gives the radial dependence of lth coefficient in the above expansion. This series has infinite terms, however only finite terms will be sufficient to represent the atomic sphere magnetisation. So the entire analysis is restricted to the atomic sphere of radius R equal to one half of the nearest neighbour distance.

Using (3) and (4) the projection operator Γ has been derived in the matrix form (Kaprzyk *et al* 1981). The matrix elements $\Gamma(h, \kappa)$ are given by

$$\Gamma(\mathbf{h}, \kappa) = V/V_0\, 1/48 \sum_g 3/R^3 \int_0^R \mathrm{d}r r^2 j_0(|\mathbf{h} - \kappa_g| r). \tag{5}$$

where V is the volume of the atomic sphere. These operators enables one to get the projected form factors corresponding to the atomic sphere magnetisation from the experimentally measured form factors.

$$\mathbf{f}_\Gamma = \Gamma \cdot \mathbf{f} = 1/\mu_{\text{bulk}}\, \Gamma \cdot \mathbf{M} = 1/\mu_{\text{bulk}}\, \mathbf{M}_\Gamma \tag{6}$$

where $\mathbf{f}_\Gamma$ and $\mathbf{f}$ are column vectors. In the forward direction,

$$\mathbf{f}_\Gamma(0) = M_\Gamma(0)/\mu_{\text{bulk}} = \mu_R/\mu_{\text{bulk}} \tag{7}$$

where μ_R is the magnetic moment corresponding to the atomic sphere magnetisation and μ_{bulk} is the magnetic moment corresponding to the ws cell.

Similarly the experimental form factors can be projected to get the spherical ($\mathbf{f}_{\Gamma_0}$) and aspherical ($\mathbf{f}_{\Gamma 4}$) parts using operator Γ_l (Kaprzyk *et al* 1981). The form of $\Gamma_l(\mathbf{h}, \kappa)$ is

$$\Gamma_l(\mathbf{h}, \kappa) = V/V_0\, K_l(\hat{h}) \left[(-1)^l 3/R^3 \int_0^R \mathrm{d}r r^2 j_l(hr) j_l(\kappa r) \right] K_l(\hat{\kappa}). \tag{8}$$

For atomic sphere magnetisation (4) can be rewritten as

$$M(\mathbf{r}) = M_0^0(r) + M_4^0(r)\, K_4(\hat{r}). \tag{9}$$

Assuming the same radial dependence for $M_0^0(r)$ and $M_4^0(r)$ an analytical expression has been derived (Kaprzyk *et al* 1981) for the aspherical form factor (f_4^{calc}) which is given by

$$\mathbf{f}_4^{\text{calc}} = \mu_R/\mu_{\text{bulk}}\, q \boldsymbol{K}_4 \cdot \mathbf{f}_0^{\text{spin}} \tag{10}$$

where $\mathbf{f}_0^{\text{spin}}$ is the spherical part of the spin-only form factor derived from the measured $\mathbf{f}$.

$$K_4(\mathbf{h}, \kappa) = V/V_0\, 1/48 \sum_g 3/R^3 \int_0^R \mathrm{d}r r^2 j_4(|\mathbf{h} - \kappa_g| r)\, K_4(\mathbf{h} - \kappa_g) \tag{11}$$

$$q = \frac{2}{(21)^{1/2}} (5\gamma/2 - 1) \left\{ 1 - \frac{g-2}{g} \frac{\mu_{\text{bulk}}}{\mu_R} \right\}$$

The asphericity parameter (γ) is refined by a least squares comparison of $\mathbf{f}_{\Gamma 4}$ and $\mathbf{f}_4^{\text{calc}}$.

3. Application of the PO formalism to NiRu alloys

Magnetic structure amplitudes in Ni_{1-x} Ru_x ($x = 0{\cdot}027$, $0{\cdot}033$ and $0{\cdot}046$) were measured using the polarised neutron diffraction techniques (I). Magnetisation measurements of these alloys yielded the bulk moments to be $0{\cdot}505(2)\ \mu_B$, $0{\cdot}473(2)\ \mu_B$

Table 1. Experimental form factors of $Ni_{1-x}Ru_x$ normalised to their bulk moment.

	Form factors		
hkl	$x = 0.027$	$x = 0.033$	$x = 0.046$
111	0·688(5)	0·643(7)	0·618(4)
200	0·596(5)	0·587(4)	0·553(5)
220	0·394(4)	0·358(6)	0·349(5)
311	0·298(3)	0·275(5)	0·228(2)
222	0·318(5)	0·276(5)	0·220(2)
400	0·151(7)	0·130(5)	0·132(5)
331	0·166(5)	0·142(4)	0·124(4)
420	0·118(7)	0·109(5)	0·105(6)
422	0·116(5)	0·096(4)	0·085(4)
511	0·044(4)	0·090(4)	0·080(4)
333	0·104(4)	0·035(3)	0·037(4)
440	0·043(7)	0·050(6)	0·053(3)
531	0·031(7)	0·022(7)	0·038(10)
600	−0·039(9)	−0·029(6)	−0·017(6)
442	0·059(6)	0·035(5)	0·041(4)
620	−0·002(9)	−0·007(7)	−0·006(7)

and 0·404(2) μ_B respectively. Form factors in each case were obtained by normalising the measured magnetic structure amplitudes to the bulk moment. Table 1 gives the neutron form factors for the alloys. This form factor corresponds to the magnetisation residing in the ws cell. In order to get the asphericity parameter and the uniform 'diffuse' magnetisation density, this form factor, in principle, should be compared to the calculated one corresponding to the magnetisation in the ws cell. Lengthy numerical integration has to be performed over a number of special directions in order to get such a form factor (Dobrzynski 1974). On the other hand it is easier to obtain an analytical expression for the form factor corresponding to the atomic sphere magnetisation. In such a case even the measured form factor should be projected into the atomic sphere and then compared with the analytical expression. This is one of the principal aspects of the projection operator formalism (Kaprzyk *et al* 1981).

Form factors given in table 1 are projected to get the total (f_Γ), spherical (f_{Γ_0}) and aspherical (f_{Γ_4}) components of form factors corresponding to the atomic sphere magnetisation. To overcome the series termination errors in using (2), ten extra terms were added to the list of observed reflections, each of them with value of zero and standard deviation equal to the geometrical average of the value of the last seven observed $f(\kappa)$'s. The projected form factors for the alloy thus obtained are given in table 2. The plot of the difference form factor Δf(alloy-Ni) for each of the three concentrations as a function of $\sin\theta/\lambda$ is given in figure 1a. By way of comparison we reproduce in figure 1b, a similar plot obtained by the previous analysis (I). When the form factor trends in NiRu alloys are compared, both the analyses show that the form factor sharpens or the magnetisation distribution becomes extended with increasing Ru concentration. However when the average magnetisation distribution with respect to pure nickel is considered, it is seen that the previous analysis shows that the form factor

Table 2. Projected form factors ($\mathbf{f}_\Gamma$, $\mathbf{f}_{\Gamma_0}$ and $\mathbf{f}_{\Gamma_4}$) for $Ni_{1-x}Ru_x$ alloys.

	$x = 0.027$			$x = 0.033$			$x = 0.046$		
hkl	$\mathbf{f}_\Gamma$	$\mathbf{f}_{\Gamma_0}$	$\mathbf{f}_{\Gamma_4}$	$\mathbf{f}_\Gamma$	$\mathbf{f}_{\Gamma_0}$	$\mathbf{f}_{\Gamma_4}$	$\mathbf{f}_\Gamma$	$\mathbf{f}_{\Gamma_0}$	$\mathbf{f}_{\Gamma_4}$
000	0·993	0·993	0·000	0·983	0·983	0·000	0·967	0·967	0·000
111	0·688	0·683	0·004	0·652	0·653	−0·002	0·633	0·633	0·000
200	0·600	0·608	−0·009	0·580	0·576	0·003	0·551	0·551	−0·000
220	0·395	0·398	0·006	0·360	0·366	0·001	0·331	0·330	0·001
311	0·295	0·301	−0·007	0·272	0·273	−0·003	0·234	0·236	−0.002
222	0·317	0·275	0·025	0·272	0·249	0·012	0·218	0·213	0·007
400	0·154	0·195	−0.049	0·144	0·174	−0·034	0·127	0·148	−0·020
331	0·165	0·152	0·020	0·145	0·135	0·016	0·129	0·117	0·010
420	0·121	0·139	−0·011	0·109	0·121	−0·009	0·105	0·108	−0·005
422	0·117	0·097	0·014	0·097	0·082	0·012	0·085	0·080	0·009
511	0·039	0·072	−0·036	0·029	0·059	−0·032	0·035	0·062	−0·024
333	0·112	0·072	0·037	0·091	0·059	0·032	0·075	0·062	0·025
440	0·045	0·041	0·012	0·045	0·031	0·010	0·056	0·038	0·009
531	0·031	0·027	0·002	0·024	0·020	0·002	0·034	0·027	0·002
600	−0·028	0·024	−0·038	−0·024	0·017	−0·030	−0·013	0·024	−0·030
442	0·048	0·024	0·018	0·031	0·017	0·014	0·038	0·024	0·014
620	0·001	0·012	−0·015	−0·003	0·007	−0·011	0·000	0·013	−0·013

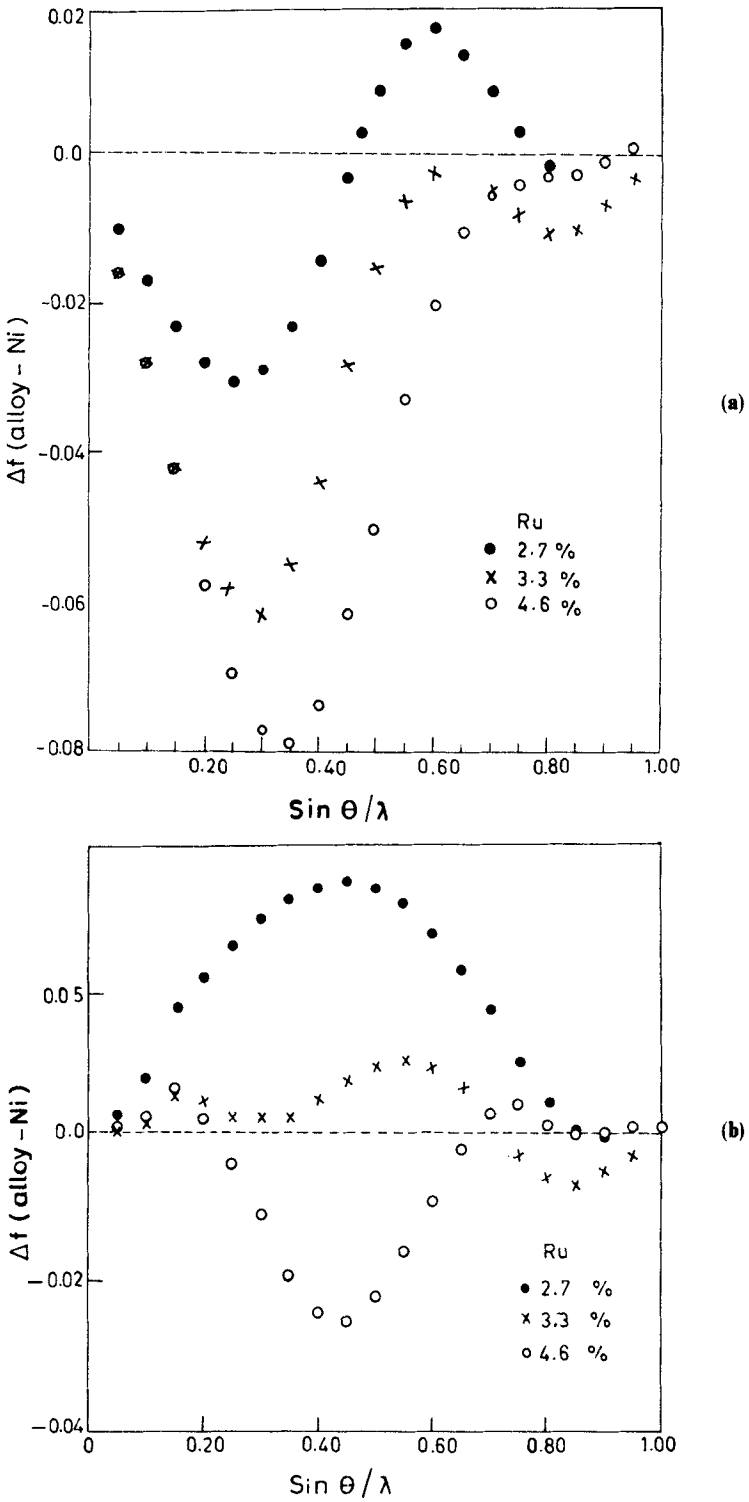

Figure 1. The difference Δf of the alloy form factor and Ni form factor obtained from **a.** present analysis, **b.** form factor analysis (I), plotted as a function of sin θ/λ.

for the alloy of lowest concentration is expanded compared to that of pure Ni thus varying the average sharpness from $-1{\cdot}8\,\%$ to $0{\cdot}6\,\%$ over the range of $\sin\theta/\lambda$ from 0 to $1{\cdot}0\,\text{Å}^{-1}$. The present analysis shows that the average sharpness varies from $0{\cdot}7\,\%$ to $3{\cdot}5\,\%$.

Due to the itinerant nature of magnetic electrons there is no unique way of defining a local moment in 3d transition metals and alloys. In an operational sense, we define the local site moment to be the moment residing in the atomic sphere. From a knowledge of the projected form factor at $\kappa = 0$ the value of the local moment can be obtained from (7). The μ_{site} values are given in table 3 together with the results of the previous analysis. μ_{site} obtained from the present analysis compare well with those obtained using a self-consistent procedure outlined in I. This method is also model-independent neither involving free ion form factors nor an assumption of uniform magnetisation at the point away from the atomic site (Moon 1971). Thus both these methods involving Fourier summation of the measured magnetic structure amplitudes give consistent μ_{site} value. However the μ_{site} values obtained from the form factor analysis (*I*) given in the last column of table 3 do not agree quantitatively with the present result. The variation of site moment with Ru concentration using the present and the form factor analysis (*I*) are given in figure 2. Over the measured range of Ru concentration, $d\mu_{\text{site}}/dc$ from the present analysis is $-5{\cdot}3\mu_B$/Ru atom. On extrapolation, the site moment variation predicts the system to become paramagnetic at ~ 12 atomic % of Ru. This corroborates with the magnetisation measurements (Sadron 1932). The form factor analysis on the other hand yields a value of $-9\ \mu_B$/Ru atom predicting the system to become paramagnetic at 8 atomic % of Ru.

In order to define the 'diffuse' magnetisation density we have taken the following approach. If any constant background magnetisation is present throughout the ws cell it should also be present in the atomic sphere. $(\mu_{\text{bulk}} - \mu_{\text{site}})$ gives the measure of the diffuse moment over the volume of the ws cell lying outside the atomic sphere. Thus one

Table 3. Local site moment in Ni_{1-x} Ru_x alloys using different analyses.

	μ_{site} (in μ_B)		
x	using PO formalism	using self consistent method (I)	using form factor analysis (I)
0·027	0·50(1)	0·49(1)	0·485(1)
0·033	0·46(1)	0·45(1)	0·422(1)
0·046	0·39(1)	0·39(1)	0·322(2)

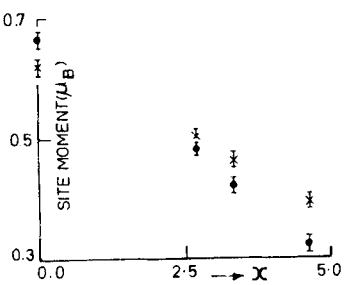

Figure 2. Variation of site moment with Ru concentration (x) (×-present analysis, •-form factor analysis (I)).

can get the uniform diffuse moment residing in the atomic sphere and find the fraction of the spin moment (α) which forms the uniform diffuse moment density inside the atomic sphere. This procedure yields values of $\alpha_{Ni} = 0{\cdot}04$ and $\alpha_{Fe} = 0{\cdot}02$. In the projection operator method when α was varied as a free parameter, the values obtained were $\alpha_{Ni} = 0{\cdot}04(4)$ and $\alpha_{Fe} = 0{\cdot}10(8)$. Our method of calculation of the diffuse moment without involving a least squares analysis agrees well with the reported value of α for Ni and Fe. The variation of the diffuse moment with Ru concentration using the present and those derived from the form factor analysis (I) is given in figure 3. Present analysis shows that the diffuse moment is very small in the alloys as in pure metals and does not vary much with impurity concentration.

Since the diffuse moment is negligible in all the alloys we assume it to be zero in further analysis. Under this assumption (10) gives the form factor corresponding to the aspherical part of atomic sphere magnetisation. Aspherical part of the projected form factor $\mathbf{f}_\Gamma$ are least squares refined by (10) varying q as a free parameter. From the refined q's the asphericity parameter can be extracted using (11). The variation of γ with Ru concentration from the present and form factor analysis are given in figure 4. In the present analysis, the asphericity parameter (γ) is the same in the alloy as also in pure Ni ($\gamma_{Ni} = 0{\cdot}20(1)$) and does not vary up to $x = 0{\cdot}033$ but for $x = 0{\cdot}046$ it becomes 0·24(1). This is in qualitative agreement with the trend given by our calculations using the coherent potential approximation (Chakravarthy and Madhav Rao 1981) which shows γ to change only beyond $x \sim 0{\cdot}06$. However the form factor analysis (*I*) shows that the asphericity parameter decreases to 0·17(1) for $x = 0{\cdot}027$ and then increases to 0·24(2) for $x = 0{\cdot}046$.

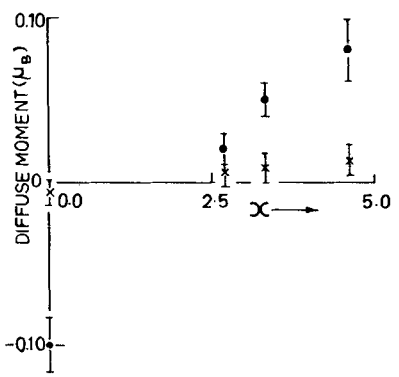

Figure 3. Variation of diffuse moment with Ru concentration (x). (symbols as in figure 2).

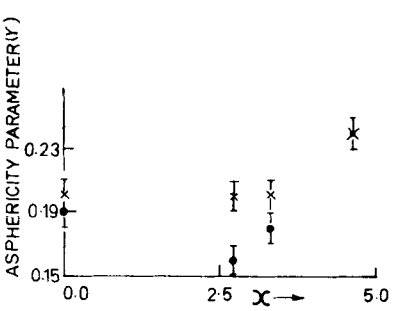

Figure 4. Variation of asphericity parameter (γ) with Ru concentration (x). (symbols as in figure 2).

Projection operator method of analysis show that μ_{site}, α and γ vary smoothly with Ru content unlike the sharp features observed using the form factor analysis. Further, the results of the PO analysis are more closer to those predicted by our CPA calculations.

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