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EXPERIMENTAL SPIN DENSITIES

R. M. Moon

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EXPERIMENTAL SPIN DENSITIES*

R. M. Moon

*Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830*INTRODUCTION

The role of neutrons in determining spin densities is roughly analogous to that of x-rays in determining charge densities. There are important differences, however, and it seems appropriate to begin by reviewing exactly what is measured in neutron diffraction experiments on magnetic materials. First of all, the elastic magnetic neutron scattering is given by the Fourier inversion of the time-averaged magnetization density, which is the sum of the spin density and the magnetic moment density due to unquenched orbital currents. In many cases of interest, like the 3d-metals, the orbital contribution is small, but it is seldom negligible; and in the rare-earth metals and compounds it is very important. We rely on other experimental techniques, or theoretical models, to tell us what fraction of the total moment is due to the orbital contribution. For a given electronic state the orbital moment density is more compact than the spin density, so that at high scattering angles the orbital contribution to the neutron scattering can be important even though the net orbital moment is a small fraction of the total moment. So, let us remember that for magnetic scattering of

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neutrons it is the magnetic moment density, not the spin density, which plays a role analogous to the charge density for x-ray scattering.

In comparing the x-ray and neutron cases, it should be emphasized that for systems with unpaired spin, the density functions for spin-up electrons may be different than for spin-down electrons. In the Hartree-Fock formalism, this comes about because the exchange terms connect electrons of the same spin state, so that the total exchange interaction is different for majority and minority spin states. Unrestricted Hartree-Fock calculations⁽¹⁾ show that the majority spin density is more compact than the minority spin density. If $\rho_i(\uparrow)$ and $\rho_i(\downarrow)$ are normalized density functions for spin-up and spin-down electrons in state i , then the spin density is

$$\rho_{sp} = \sum_i [n_i(\uparrow)\rho_i(\uparrow) - n_i(\downarrow)\rho_i(\downarrow)], \quad (1)$$

and the charge density is

$$\rho_{ch} = \sum_i [n_i(\uparrow)\rho_i(\uparrow) + n_i(\downarrow)\rho_i(\downarrow)], \quad (2)$$

where the n_i is an occupation number and the sum runs over all electronic states. These equations may be rewritten in the more suggestive form,

$$\rho_{sp} = \sum_i [n_i(\uparrow) - n_i(\downarrow)]\rho_i(\uparrow) + \sum_i n_i(\downarrow)[\rho_i(\uparrow) - \rho_i(\downarrow)], \quad (3)$$

$$\rho_{ch} = \sum_i [n_i(\uparrow) + n_i(\downarrow)]\rho_i(\uparrow) - \sum_i n_i(\downarrow)[\rho_i(\uparrow) - \rho_i(\downarrow)]. \quad (4)$$

The second sums in the above equations are small but are not completely negligible. For the spin density, note that the first sum vanishes for all closed shell electrons, while for moderately heavy atoms it is the

core which dominates the charge density. Therein lies the major advantage in the use of neutrons for investigating the behavior of the outer electrons.

Another important difference in the neutron and x-ray cases is the vector nature of the magnetization and of its Fourier transform, the magnetic scattering amplitude. It is this vector amplitude which is analogous to the x-ray form factor. The magnetic amplitude is given by

$$\vec{p}(\vec{k}) = \frac{\gamma e^2}{2mc^2} \int e^{i\vec{k} \cdot \vec{r}} \vec{M}(\vec{r}) d^3r, \quad (5)$$

where $\vec{k}$ is the scattering vector, γ is the neutron moment in nuclear magnetons and $\vec{M}(\vec{r})$ is the electronic magnetic moment density. The cross section for elastic scattering from an assembly of atoms with the neutron going from an initial spin state s to a final spin state s' is

$$\frac{d\sigma}{d\Omega}^{ss'} = |\langle s' | \sum_i e^{i\vec{k} \cdot \vec{r}_i} (b_i + B_i \vec{I}_i \cdot \vec{\sigma} + \vec{p}_{\perp i} \cdot \vec{\sigma}) | s \rangle|^2, \quad (6)$$

where $\vec{p}_{\perp} = \hat{k} \times (\vec{p} \times \hat{k}), \quad (7)$

where b is the nuclear coherent amplitude, B is the spin-dependent nuclear amplitude, $\vec{\sigma}$ is the neutron spin operator and the sum extends over all atomic sites $\vec{r}_i$. The vector $\vec{p}_{\perp}$ is the component of $\vec{p}$ which is perpendicular to the scattering vector. Only those components of $\vec{M}(\vec{r})$ which are perpendicular to $\vec{k}$ are effective in scattering neutrons. Recalling the properties of the Pauli spin matrices, we see from Eq. (6) that the component of $\vec{p}_{\perp}$ parallel to the neutron polarization gives non-spin-flip

scattering and the components of $\vec{p}_\perp$ normal to the neutron polarization give spin-flip scattering. To gain the maximum information about $\vec{M}(\vec{r})$ we should have an experimental arrangement which allows the measurement of each of these cross sections. In the next section we consider the various experimental techniques which have been used in the study of magnetic neutron scattering.

EXPERIMENTAL TECHNIQUES

To simplify the discussion, let us assume we are dealing with a simple ferromagnet with no nuclear polarization and only one type of atom per unit cell. For Bragg scattering the partial cross sections of Eq. (6) then become

$$\frac{d\sigma^{\pm\pm}}{d\Omega} \sim (b \pm p_{\perp z})^2, \quad (8)$$

$$\frac{d\sigma^{\pm\mp}}{d\Omega} \sim p_{\perp x}^2 + p_{\perp y}^2, \quad (9)$$

where the z axis is along the neutron polarization direction (parallel to the net sample magnetization) and the y axis is perpendicular to both the neutron polarization and the scattering vector. We will start with the simplest experiment and proceed toward complexity. It is true that the information content rises with complexity but, unfortunately, the number of neutrons into the detector drops rather precipitously.

Case I - Unpolarized beam, no analysis of diffracted beam, $\hat{z} \cdot \hat{K} = 0$. To obtain the Bragg intensity we must sum the partial cross sections over initial and final neutron spin states,

$$I \sim \sum_{s,s'} \frac{d\sigma^{ss'}}{d\Omega} \sim b^2 + p_z^2 + p_y^2. \quad (10)$$

This experiment is sometimes useful for $p \approx b$, which is the case for the inner reflections in some materials, but for the outer reflections where $p \ll b$, the magnetic contribution is overwhelmed by the nuclear contribution. In general, we would like to be able to make significant measurements in the region where $p/b \approx 0.01$.

Case II - Polarized beam, no analysis of diffracted beam, $\hat{z} \cdot \hat{k} = 0$. This is the standard polarized beam experiment,⁽²⁾ in which the intensity of a Bragg peak is measured as a function of the direction (+ or -) of beam polarization. The intensities for (+) and (-) initial spin states are obtained by summing the partial cross sections over the final spin states,

$$I^{\pm} \sim \sum_s \frac{d\sigma^{ss'}}{d\Omega} \sim (b \pm p_z)^2 + p_y^2. \quad (11)$$

The "flipping ratio" is given by

$$R = \frac{I^+}{I^-} = \frac{(b + p_z)^2 + p_y^2}{(b - p_z)^2 + p_y^2}. \quad (12)$$

The flipping ratio can be determined to very high statistical accuracy and its sensitivity to small values of p_z is greatly enhanced over Case I. In the 3d-ferromagnets which have been measured with this technique, the assumption is made that $\vec{M}(\vec{r})$ is everywhere collinear, or that $p_y = 0$. Blume⁽³⁾ has suggested that this may not be true, in which case the polarized beam experiments should be reinterpreted. In my opinion, if $p_y \neq 0$ for the 3d metals, then at least $p_y/b \ll 1$. In this case the observed flipping ratios are very insensitive to p_y and the data probably need not be reconsidered. This technique has the great advantage that

each observation is self-calibrating, provided we know the nuclear amplitude. Factors related to incident intensity, absorption and the scattering geometry cancel out of the ratio. The same is true of the Debye-Waller factor, provided the electrons follow the nuclei in their thermal vibrations. Peak intensities, rather than integrated intensities, are usually measured to make optimum use of counting time. Of course, we must have a nearly extinction-free sample and there are small corrections to be made for imperfect beam polarization and imperfect flipping.

Case III - Polarized beam, polarization analysis after the sample, $\hat{z} \cdot \hat{K} = 0$. This is the way the flipping ratio measurements should really be performed. The polarization analysis technique has been described by Moon, Riste and Koehler.⁽⁴⁾ With flippers before and after the sample we could measure

$$R = \frac{I^{++}}{I^{--}} = \frac{(b + p_z)^2}{(b - p_z)^2} \quad (13)$$

by observing the Bragg intensity with both flippers off and with both flippers on. By turning only one of the flippers on we could measure

$$I^{+-} = I^{-+} \sim p_y^2. \quad (14)$$

This experiment has not been performed yet.

Case IV - Polarized beam, polarization analysis after the sample, $\hat{z} \cdot \hat{K} = 1$. In this arrangement we turn off the principal magnetic scattering by magnetizing along $\vec{K}$ and this should be the most useful method for detecting a non-collinear component in $\vec{M}(\vec{r})$. With a single flipper before the sample the ratio of "on" to "off" intensities would be

$$R = \frac{I^{-+}}{I^{++}} = \frac{p_x^2 + p_y^2}{b^2} . \quad (15)$$

This experiment has been performed for hexagonal Co with a null result.⁽⁵⁾ However, Blume⁽⁶⁾ has pointed out that for the particular reflections studied, the transverse spin components should vanish by symmetry, so the issue is still not resolved.

Case IV also has important applications for antiferromagnetic Bragg scattering and for diffuse elastic scattering from paramagnets and antiferromagnets. In this geometry all magnetic scattering is spin-flip scattering and all nuclear scattering, except for nuclear spin incoherence, is non-spin-flip scattering. We can achieve a nearly complete separation of nuclear and magnetic scattering, which is very important if accurate values of magnetic scattering amplitudes are desired. An example of this technique used to measure the diffuse elastic scattering from paramagnetic Gd_2O_3 is shown in Fig. 1.

We turn now to a discussion of important experimental results, largely determined as in Case II above.

RARE EARTHS

Many of the complications discussed previously in relating the magnetic neutron scattering to the electron density are not present in the case of Gd. The 4f shell is half-filled resulting in no orbital moment and a total spin of 7/2. The core contribution to the spin density has been estimated and may be neglected for our purposes. Since there are no spin-down electrons in the 4f shell, the 4f spin density and charge density should be identical. Metallic Gd orders ferromagnetically at

293°K and has a saturation moment of $7.55 \mu_B/\text{atom}$.⁽⁷⁾ From the 4f electrons we expect $7.0 \mu_B/\text{atom}$ and it is generally acknowledged that the $0.55 \mu_B$ excess moment must come from spin polarization in the 5d and 6s conduction bands. So we expect a spin density which is dominated by well-localized 4f electrons with a small contribution from diffuse conduction electrons.

The major difficulty in doing neutron experiments on Gd is that the natural element is opaque to neutrons. At Oak Ridge, we have recently grown single crystals of the low-capture isotope ^{160}Gd , and have determined the spin density with high accuracy.⁽⁸⁻⁹⁾

The experimental results are shown in Fig. 2. The quantity μf is related to the magnetic scattering amplitude by

$$\mu f = \left(\frac{2mc^2}{ye^2} \right) P, \quad (16)$$

and is equal to the integral in Eq. (5). These measurements were made at a temperature of 96°K and an applied field of 12.5 kOe. Under these conditions the saturation moment is $6.92 \mu_B$ ⁽⁷⁾ and we expect a 4f moment of $6.42 \mu_B$, assuming the 4f moment has the same temperature dependence as the total moment. The smooth behavior of the experimental points at high angles indicates a spherically symmetric spin distribution, as is expected for an $L = 0$ ion. The solid line is the 4f form factor of Blume, Freeman and Watson⁽¹⁰⁾ normalized to $6.42 \mu_B$. This is based on a non-relativistic Hartree-Fock calculation for the free +3 ion and is not in good agreement with the data.

The behavior of the low-angle peaks is shown in Fig. 3 on a different scale. The positive curvature over the first three points is not

characteristic of atomic form factors and strongly suggests that we are seeing a conduction electron contribution. We have attempted to make a separation of the 4f and conduction contributions based on very simple and general ideas about how these two contributions should behave. Specifically, we assumed that in real space the 4f contribution shows no overlap between atoms and the conduction contribution varies slowly with $\vec{r}$ so that it has no significant Fourier components beyond the third Bragg peak. We then tried to adjust the amplitudes for the first three peaks so that when they were combined with the rest of the data in a Fourier inversion, a flat spin density was produced in the region between atoms, satisfying our criterion for local behavior. This was particularly easy to do in a basal plane projection because there is a natural hole in the hcp structure through which the outer spin density can be examined and because only the first Bragg amplitude had to be varied. The results of such a calculation for three different values of the (010) amplitude are shown in Fig. 4. We have used an orthorhombic unit cell and a spherical averaging technique⁽¹¹⁾ to reduce series termination errors. The top curve shows the projection of the spherically averaged density along the line shown in the structural diagram when the observed (010) amplitude is used. It is clear that this density does not have the desired local character. For the second curve the (010) amplitude has been decreased to fall on the linear extrapolation indicated in Fig. 3. Beautiful localized behavior is now evident. Furthermore, the agreement between the flat density value and the zero level if the total moment were $6.42 \mu_B/\text{atom}$ indicates that the integral under our "local" density function is just what we expect for the 4f electrons. The third

curve is included to give some idea of the sensitivity of the method. Here the (010) amplitude has been moved below the linear extrapolation in Fig. 3, and the result clearly does not satisfy our criterion for local behavior. The integral of the spin density above the flat region in Fig. 3b has been calculated by the procedure described by Moon⁽¹¹⁾ to be $6.44 \pm 0.16 \mu_B$, in excellent agreement with the expected 4f moment of $6.42 \mu_B$. It is this agreement which gives us some confidence that our local form factor does indeed describe the 4f electrons. An interesting contrast between the total density and the local density is shown in the contour maps of Fig. 5. Only the (000) and (010) amplitudes were changed in going from the total moment projection to the local moment projection.

Let us turn to an examination of the diffuse component. The Fourier amplitudes are given by the difference between the observations and our local amplitudes and are displayed in the insert of Fig. 3. Contour maps showing the inversion of these amplitudes are given in Fig. 6 for several principal planes. We see a positive density at the atomic sites and a negative density in the region between atoms. This negative polarization is found in slowly undulating columns which run continuously through the lattice parallel to the c axis. Theoretical calculations are not sufficiently advanced to judge whether our diffuse component behaves as conduction electrons should. However, the diffuse component is certainly long range and oscillatory, which are properties universally attributed to conduction electrons in the rare-earth metals.

We come now to the interesting question of why the Watson-Freeman wave functions fail in the metallic case. The two most obvious reasons

are that they considered the nonrelativistic case and their calculations were for the free ion. The presence of the conduction electrons in the metal would provide additional screening and allow the 4f electrons to move in slightly larger orbits. We sought an experimental answer to this question by measuring the paramagnetic form factor of Gd_2O_3 , with the idea that the oxide would provide a closer approximation to the free ion than in the metallic case. Our results are shown in Fig. 7, together with the metallic results and the Blume-Watson-Freeman form factor. We see that the oxide results are consistently higher than the metallic form factor and are in good agreement with the nonrelativistic free-ion calculation. However, on the theoretical side, Davis and Cooke⁽¹²⁾ undertook a series of atomic calculations, using a Hartree-Fock-Slater program, to test the sensitivity of the 4f wavefunctions to the presence of electrons in the 6s or 5d levels. They found a negligible change in the 4f form factor in going from the neutral atom ($4f^7 5d^1 6s^2$) to the +3 ion ($4f^7$). This is a strong indication that screening by the conduction electrons is not important in determining the radial wavefunctions in the metal. Furthermore, they found that with a reasonable value for the Slater exchange coefficient, their form factor was in very good agreement with our metallic results, as shown in Fig. 8. More recently, relativistic Dirac-Fock wavefunctions for Gd^{3+} have been obtained by Desclaux and Freeman,⁽¹³⁾ and these also yield a 4f form factor in good agreement with our metallic results. We seem to be in good shape theoretically to explain the metallic results but what about the oxide case? Although a serious calculation has not yet been attempted, it is believed that the oxide form factor is affected by covalent bonding. (12-13)

Experimental results on Tb by Steinsvoll et al.⁽¹⁴⁾ and on Tm by Brun and Lander⁽¹⁵⁾ are qualitatively similar to the Gd results. The metallic form factor in each of these cases indicates a 4f density which is expanded in comparison with the nonrelativistic Hartree-Fock calculations. It seems likely that proper relativistic calculations would be in good agreement with the experimental results in all three cases.

I should like to mention one more rare-earth case which is intriguing because of its novelty. Unpolarized beam experiments are now in progress at Oak Ridge⁽¹⁶⁾ on metallic Sm, which is a rather complicated antiferromagnet. There are two different sites, ordering at different temperatures, which have roughly the same atomic magnetic form factor. Because of the large magnetic unit cells, the first Bragg peak comes at a very small scattering angle ($\sin\theta/\lambda = 0.04$). The scattering amplitudes tend toward zero in the forward direction, indicating a net atomic moment which is close to zero. In the free Sm^{+3} ion the orbital and spin moments are directed oppositely, giving a net moment of $0.714 \mu_B$. In the metal, we believe that the near zero moment comes from a combination of crystal field effects, which reduce the ionic moment, and conduction electron spin polarization parallel to the 4f spin. The combination of 4f and conduction spin polarization almost exactly cancels the 4f orbital moment, giving a magnetization density which oscillates in such a way that the average density nearly vanishes.

3d METALS

The problem of analyzing neutron amplitudes in terms of 3d and conduction electron contributions is much more difficult than the corresponding problem in Gd. We have no good theory to tell us what the 3d moment should be, nor do the neutron amplitudes give any hint of anomalous

behavior in the low angle region. Prior to the neutron measurements by Shull and coworkers,⁽¹⁷⁻²⁰⁾ band calculations by Wood⁽²¹⁾ and Stern⁽²²⁾ showed that large differences in the radial wavefunctions should be expected between states at the top and bottom of the 3d band. If this effect were combined with different radial functions for spin-up and spin-down electrons, the result would be complicated and very difficult to calculate. So there was no reliable theoretical prediction for the 3d spin density. For conduction electrons the situation was even more complicated. Direct exchange between 3d and 4s electrons would produce a positive 4s polarization (parallel to the 3d polarization), while s-d hybridization would tend to produce the opposite effect.⁽²³⁾ The theorists could not tell us which effect was dominant.

Fourier inversions of the neutron results showed densities with definite departures from spherical symmetry for Fe,⁽¹⁷⁾ Ni⁽²⁰⁾ and FCC Co,⁽²⁴⁾ while hexagonal Co⁽¹⁸⁾ was nearly spherically symmetric. In all cases the magnetic moment density in the region between atoms was opposite in direction to the net magnetization. The amazing thing about these results is that they can be duplicated accurately by a model in which free-atom spin-polarized Hartree-Fock density functions are superimposed on a negative constant density. For the cubic cases there are two adjustable parameters in the model, a scale factor which determines the magnitude of the total 3d spin and another parameter which determines the relative proportion of unpaired electrons with E_g and T_{2g} symmetries. Comparison of the total 3d moment with the observed magnetization determines the magnitude of the negative constant. That this model produces really excellent fits is illustrated in Fig. 9 for Co and Fig. 10 for Ni.

Another approach to the analysis of these results has been described by Moon.⁽¹¹⁾ Here the position is adopted that if you want to analyze the shape of the spin density, you can ignore the magnetization measurement (or the F_{000} structure factor) since it merely adds a constant value to the Fourier series describing the density. The neutron amplitudes were self-normalized by calculating the integral of the magnetic moment throughout the unit cell above the moment value at the point of lowest density. These "atomic" moments obtained by direct operations on the Fourier series describing the magnetization are compared in Table I with the 3d-like moments obtained earlier by fitting free-atom form factors to the data and with the magnetization results. This calculation was then followed by a spherical average and a self-consistent correction for the orbital contribution. The final result was a normalized form factor describing the shape of the spatially varying part of the spin density. These form factors are compared with the Watson-Freeman free atom calculations in Fig. 11. The agreement is remarkable and was achieved with no adjustable parameters. So again we are led to a model in which 3d-like lumps of spin density, which have more moment than expected, are sitting in a sea of negative polarization.

The success of this simple model has perhaps led people to ascribe more significance to it than it merits. It provides an accurate description of the total spin density, but one should not conclude that it provides separate descriptions of the 3d and 4s spin polarizations. All band calculations show that the situation is much more complex than is suggested by this simple model. The success of the model in describing experimental results must be regarded as fortuitous.

There have been a number of band calculations aimed at an explanation of the neutron results. The case of Fe has been considered by Wakoh and Yamashita,⁽²⁵⁾ DeCicco and Kitz⁽²⁶⁾ and Duff and Das.⁽²⁷⁾ Hexagonal Co has been considered by Hodges and Ehrenreich⁽²⁸⁾ and Ni by Hodges, Ehrenreich and Lang.⁽²⁹⁾ In general, the band calculations are quite successful in duplicating the observed anisotropies. In regard to the radial spin density and the question of conduction electron polarization, the theoretical position is still ambiguous.

Probably the best agreement between experiment and theory was achieved by DeCicco and Kitz⁽²⁶⁾ who calculated the magnetic scattering amplitudes for the total spin density in Fe. However, they made no analysis of separate 3d and 4s contributions. Wakoh and Yamashita⁽²⁵⁾ calculate separate 3d and 4s magnetic form factors and analyze their total spin density in terms of these contributions. The total form factor is written as

$$f_{\text{spin}} = (1 + \xi)f_{3d} - \xi f_{4s}. \quad (17)$$

They obtain $\xi = 0.035$, in contrast to the value of 0.10 obtained by Shull and Yamada in fitting their observations with free atom form factors. A comparison of experimental and theoretical form factors for the total spin density is shown in Table II for the inner reflections. We note that the Wakoh and Yamashita form factor is in rather poor agreement with the experimental results in the low angle region and that much better agreement can be obtained using their 3d and 4s form factors but with $\xi = 0.1$.

It is difficult to make a quantitative comparison with the Duff and Das⁽²⁷⁾ results because they did not compute the scattering amplitudes. In analyzing their calculated spin density, they were unable to make a

definite statement about the sign or magnitude of the 4s polarization. If the spherical part of their spin density is compared with the spherical average of the Fourier inversion of the experimental data, one finds that their spin density is significantly expanded relative to the experimental results.

In the work on Ni by Hodges et al.⁽²⁹⁾ various experimental results are used to determine theoretical parameters. When the sign and magnitude of the s-d interaction is determined by results on the ferromagnetic Kerr effect, a small positive conduction electron polarization is predicted. However, the resulting neutron form factor is in poor agreement with the experimental results for the inner reflections. Good agreement with the neutron results can be obtained by reversing the sign of the s-d interaction.⁽³⁰⁾ In the unrestricted Hartree-Fock band calculation by Connolly⁽³¹⁾ for Ni, no spin densities were calculated but he did find a net negative conduction electron polarization.

In my opinion, none of these band calculations is convincing in regard to the sign and magnitude of the conduction electron polarization. I believe that it is also true that none of the band calculations give a spin density which agrees with the neutron results as well as does the simple free atom plus negative constant model.

The case of antiferromagnetic Cr should also be mentioned. The experimental results⁽³²⁾ were in rather good agreement with a free atom form factor. A band calculation by Asano and Yamashita⁽³³⁾ correctly predicted the observed asymmetry and gave good agreement with the radial spin density.

There have been many other experiments involving 3d compounds and alloys. Some of these are reviewed in the surveys by Nathans⁽³⁴⁾ and

Paoletti.⁽³⁵⁾ One particularly interesting topic involving 3d compounds is reviewed in the next section.

COVALENCY

The neutron should be especially useful as a tool in studying covalency effects in transition metal compounds because it responds to the outer electron configuration. Hubbard and Marshall⁽³⁶⁾ have given a theory which accounts for the main features observed in many cases. The principal effect is a reduction in the cation moment due to spin transfer to the ligand. The remaining spin density is contracted relative to the free-ion distribution. The classic example of this type of behavior is found in the work on NiO by Alperin⁽³⁷⁾ who found a 3d-like moment only 82% of that expected for Ni^{2+} . There have been several determinations⁽³⁸⁻⁴¹⁾ of covalency parameters based on the interpretation of Bragg intensities from antiferromagnets using the theory of Hubbard and Marshall. Of particular interest is the work by Hutchings and Guggenheim⁽⁴¹⁾ who attempted a critical comparison between theory and experiment. The general behavior predicted by the simple Hubbard and Marshall theory was confirmed in a much more sophisticated calculation by Ellis, Freeman and Ros⁽⁴²⁾ in which they treated an $(\text{NiF}_6)^{4-}$ cluster by a molecular-orbital self-consistent-field method.

A major flaw in this generally satisfactory situation was the longstanding observation⁽⁴³⁾ that, in a number of compounds, Mn^{2+} ions show a negligible loss of moment and their spin density is expanded relative to the free-ion calculations. The simple theory would require that if there were no spin transfer the density should be the same as in the free ion. The cluster calculations by Freeman and Ellis⁽⁴⁴⁾ on $(\text{MnF}_6)^{4-}$ seem

to resolve this difficulty and demonstrate the inadequacy of the simple theory for some cases. They indeed find an expanded spin density for this cluster.

A very interesting feature of both the simple theory and the cluster calculation on $(\text{NiF}_6)^{4-}$ has not yet been observed experimentally. The spin density transferred to the ligand is really lost only in simple anti-ferromagnetic structures where it vanishes by cancellation. In an isolated cluster or a disordered solid this ligand spin density should cause a sharp increase in the magnetic form factor as the scattering angle goes to zero. Probably the best way to see this effect is by measuring the elastic diffuse scattering in a disordered system with negligible magnetic short range order.

NEW DIRECTIONS

Many laboratories will soon be equipped to do polarized beam experiments with a superconducting magnet at the sample position. This should allow accurate Bragg scattering measurements to be made on many paramagnets, thus significantly broadening the area of application of the standard polarized beam technique.

The polarization analysis technique holds great promise as a tool for measuring elastic diffuse scattering, as in the Gd_2O_3 experiment mentioned earlier. It allows the purely magnetic diffuse scattering to be separated from most other sources of diffuse scattering (phonon, multiple Bragg, nuclear disorder, isotopic incoherence). Only the nuclear spin incoherent scattering remains to complicate the spin-flip scattering pattern. The technique suffers from low counting rates but with the advent of higher-flux reactors and better polarizing crystals it should find many applications.

The forward peak predicted in the covalency problem is one obvious application.

Another new application of the polarized beam has been pioneered by Steinsvoll⁽⁴⁵⁾ and is being currently pursued at Oak Ridge. In a ferromagnet, the same polarization dependence which has been exploited for the Bragg peak measurements is also present for the coherent phonon peaks. By constructing a triple-axis polarized-beam instrument, flipping ratio measurements can be performed on phonons. Magnetic scattering amplitudes can then be measured at any point in reciprocal space, not just at the Bragg positions. Current plans call for measurements on Ni, Fe and Gd. The hope is to obtain accurate magnetic amplitudes at small momentum transfers (inside the first Bragg peak) where conduction electron effects should be observable. A major difficulty is that the phonon intensity depends on the square of the momentum transfer, so that we will have serious intensity problems. Theoretical difficulties in interpreting the precise meaning of these amplitudes will also have to be overcome.

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TABLE I - Summary of room temperature atomic moment results

Metal	Bohr Magnetons		
	Series	Form Factor	Magnetization
Fe	2.37 ± 0.04	2.39	2.177
Co	1.96 ± 0.04	1.99	1.707
Ni	0.68 ± 0.02	0.67	0.583

TABLE II - Comparison of observed and calculated low-angle form factors for spin density in Fe. The experimental data of Shull and Yamada have been corrected for the small orbital contribution. The calculated form factors are by DeCicco and Kitz (DK) and Wakoh and Yamashita (WY). The (WYF) column is an attempt to fit the data using the 3d and 4s form factors of WY with a larger negative 4s polarization.

hkl	f(EXP.)	f(DK)	$\xi=0.035$ f(WY)	$\xi=0.1$ f(WYF)
000	1.000	1.000	1.000	1.000
110	0.625 ± 0.004	0.616	0.582	0.619
200	0.397 ± 0.001	0.389	0.376	0.402
211	0.242 ± 0.001	0.235	0.223	0.236
220	0.165 ± 0.002	0.154	0.143	0.150
310	0.130 ± 0.001	0.123	0.117	0.122
222	0.053 ± 0.001	0.053	0.049	0.051

FIGURE CAPTIONS

- Fig. 1 - Polarization-analysis pattern of $^{160}\text{Gd}_2\text{O}_3$. With the flipper off only nuclear scattering is detected; with the flipper on, only paramagnetic scattering is detected. In a conventional unpolarized beam experiment the two patterns would be superimposed. Note that useful paramagnetic data is obtained even at the Bragg peak positions.
- Fig. 2 - Magnetic-scattering amplitudes of ^{160}Gd at 96°K. Errors are smaller than the size of the data points. The line is the calculation of Blume, Freeman and Watson for Gd^{3+} , normalized to $6.42 \mu_B$.
- Fig. 3 - Magnetic-scattering amplitudes for low-angle reflections in ^{160}Gd . Experimental errors are given by the size of the data points. The insert shows scattering amplitudes for the diffuse component, believed to be due to conduction electron polarization.
- Fig. 4 - Projection of spherically averaged moment density onto basal plane as a function of distance from atomic site. The averaging sphere, of radius $0.63 \text{ \AA}$, is moved along the line indicated in the structural diagram. In (a), $(\mu f)_{010} = 5.854$; in (b), $(\mu f)_{010} = 5.400$; and in (c), $(\mu f)_{010} = 4.945$. Inserts show density near the center of the cell on an expanded scale. Dashed lines show the zero density level if the average moment per atom is $6.42 \mu_B$. Error bars show the standard deviation obtained by combining the statistical errors in individual scattering amplitudes.
- Fig. 5 - Contour maps of spherically averaged projected total and local-moment density. The projection is on the basal plane, and the radius of the averaging sphere is $0.63 \text{ \AA}$ (0.1 in Y lattice units).

The numbers on the contour lines are in units of $\mu_B/\text{\AA}^2$. Between atomic sites in the total moment projection the moment density goes negative; in the local-moment projection it is zero within experimental error over a considerable distance.

Fig. 6 - Contour maps of diffuse component of magnetic moment density.

Shaded areas have negative density values. Numbers on contour lines are multiples of $0.01 \mu_B/\text{\AA}^2$ or multiples of 1.16 kG. Atomic sites are indicated by black circles. Errors vary from $\frac{1}{2}$ contour interval to about a full interval.

Fig. 7 - Magnetic form factor of $^{160}\text{Gd}^{3+}$ as measured by the paramagnetic scattering from $^{160}\text{Gd}_2\text{O}_3$. The solid line is the Blume-Freeman-Watson form factor. The closed circles show the experimental 4f form factor measured on the metal.

Fig. 8 - Comparison of the 4f experimental form factor with calculation.

The curve labeled Davis-Cooke is based on Hartree-Fock-Slater wave-functions. The curve labeled least-squares fit was obtained by varying parameters in the Freeman-Watson 4f orbitals.

Fig. 9 - Comparison of experimental results for hexagonal cobalt with a scaled free-atom form factor. The three terms in the calculation represent the spin contribution scaled by the factor 1.18, the orbital contribution and the core contribution. The spin form factor is based on a $3d^7 4s^2$ spin-polarized Hartree-Fock calculation by Watson and Freeman. Very small corrections to the experimental data have been applied to remove the effects of asphericity.

Fig. 10 - Comparison of experimental results for Ni with a scaled free-atom form factor. The spin scaling factor was 1.19 and the T_{2g} population

was 81%. The spherical part of the spin form factor was based on a spin-polarized Hartree-Fock calculation for Ni^{2+} .

Fig. 11 - Comparison of experimental and theoretical form factors. The points represent the spin part of the spherically averaged "atomic" form factor, obtained from experimental data as described in Ref. 11. The solid curves are the Watson-Freeman spin-polarized 3d form factors for the free atom (free +2 ion in the case of Ni).

Gd_2O_3 Polarization Analysis Pattern.

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 7

FIG. 11