ELECTRON DENSITY AND SPIN DENSITY STUDIES (*)

P. J. BROWN

Institut Laue-Langevin, Grenoble, France

(Received 29 December 1981)

ABSTRACT — The paper reviews some of the problems encountered in the measurement and interpretation of electron-density measurements. The experimental problems are compared with those encountered in parallel studies of spin density distributions. To illustrate this comparison an outline of the polarized neutron technique for spin density determinations is given. Finally two examples of spin density determinations are described to illustrate the application of the techniques.

1 — INTRODUCTION

The aim of the present paper is to review some of the problems which are currently faced by experimentalists who use X-ray and neutron scattering techniques to study the electron densities in crystalline solids. It will start by reviewing some experimental problems which must now be overcome in studies of charge densities in materials containing elements outside the first two rows of the periodic table. The second part of the paper shows how some of these problems can be alleviated in measurements of spin rather than charge density and outlines the theoretical and experimental basis of spin density measurements using polarized neutrons. In the last section of the paper two examples of recent studies using the polarized neutron technique are presented.

(*) Invited talk delivered at the VII Iberoamerican Congress of Crystallography (21-26 September 1981, Coimbra, Portugal).

2 — CHARGE DENSITY MEASUREMENTS

In this discussion of charge density measurements it is assumed that the reader is familiar with the X-ray scattering techniques used in recording diffraction intensities suitable for charge density studies and has some knowledge of the methods used in their analysis. In this section some of the questions currently being debated with regard to such measurements, both of an experimental and a more philosophical nature will be discussed.

2.1 — *Experimental Problems*

2.1.1 — Range of applicability

In almost all cases the purpose of making charge density measurements is to determine in what way the electron density is modified when an assembly of free atoms is brought together to form a crystal. To a first approximation only the valence or outer shells of the atoms are modified in this process, so that only these electrons can be said to be of interest. On the other hand all the elctrons in the crystal contribute to the scattered X-ray intensity so that the fraction of the scattering contributed by the valence electrons goes down as the atomic number of the constituent goes up. Until recently, except in a very few cases, meaningful charge density studies were restricted to compounds of elements in the first two rows of the periodic table. Now, with improved accuracy in the diffraction measurements, studies of crystals containing first period transition metals, or even heavier elements are attempted. It seems unlikely that X-ray diffraction will ever be a very suitable technique to study charge densities of materials in which the electrons of interest comprise less that about 5 % of the total.

2.1.2 — Determination of the Scale Factor

The scale factor in a charge density investigation is an important parameter since it fixes the absolute values of charge density. In many studies the scale factor is left as a variable of the least squares refinement and this appears to be a valid procedure for crystals containing light atoms in which the temperature parameters have been fixed using neutron diffraction measurements. In such a case the derivation of the scale factor depends on the assumption that the scattering at high angles is correctly given by the sum of the free atoms form factors. Such a procedure may no longer be valid for heavier atoms such as transition metals in which the valence electrons may still give some contribution to the scattering at the limit of measurement.

2.1.3 — Temperature Factors

The classical technique for charge density determination pioneered by Coppens [1] and known as the X-n technique relied on obtaining accurate temperature and thermal parameters from a neutron diffraction study. These were then used as a basis to calculate the X-ray structure factors corresponding to the sum of free atoms. Fourier transformation of their differences from the observed X-ray structure factors then gave the so-called X-n map. An alternative technique is to use the higher angle X-ray data to derive the positional and thermal parameters, and this then leads to an «X-X» map. Each of these techniques has its problems; for example there are sometimes significant differences between the temperature factors derived from neutron and X-ray experiments, this will give rise to important features on the X-n map which are not due to valence electrons. On the other hand temperature factors of light atoms from high angle X-ray data may not be sufficiently precise, and with heavier atoms temperature factors may become correlated with valence electron deformations. These problems become much less acute if the X-ray measurements have been made on an absolute scale.

2.1.4 — Extinction

The recent treatments of extinction by Becker and Coppens [2], [3] and Thornley and Nelmes [4] make it possible to describe the extinction properties of the crystal by a relatively small number of parameters which can be fitted in the least squares refinement. These extinction models seem to work quite well even in the case of relatively large extinction. They can probably be used with confidence to correct extinction in a charge density study as long as it does not reduce the observed intensities by more than about 20 %. The refined parameters are of very doubtful significance.

2.1.5 — Multiple Scattering

Multiple scattering is closely related to extinction since both involve repeated Bragg scattering. It is unlikely that multiple scattering will pose a severe problem in a crystal for which the extinction is small. The presence of multiple scattering may be revealed by inequivalence of equivalent reflections or the occurrence of significant intensity in space group absences. Where detected it may be possible to avoid it by making measurements at different wavelengths or by rotating about the scattering vector.

2.1.6 — Thermal Diffuse Scattering

The inclusion of significant amounts of thermal diffuse scattering (TDS) in integrated intensity measurements, particularly at high angles is unavoidable. Under favourable circumstances (Cooper and Rouse [5], Rouse and Cooper [6], Cochran [7]) it may only lead to errors in the temperature factors and may be one of the reasons why temperature factors derived from X-ray and neutron diffraction studies do not agree. It should be borne in mind that the amount of TDS included in an integrated intensity measurement depends on the scan width and slit sizes, and is less important in an experimental set-up that gives good resolution at high angles.

2.2 — *Presentation of the Results of Charge Density Studies*

2.2.1 — Fourier Techniques

The most straightforward method of presenting the results of a study of charge density is as a Fourier synthesis, the coefficients in the synthesis being differences between the observed X-ray structure factors and a model based on positional and thermal parameters from neutron (X-n), or high angle X-ray (X-X) data. Such maps, whilst demonstrating in a clear way the spatial features of the valence electron density such as delocalisation along a bond or lone-pair densities, suffer from deficiencies in the experimental data. They are of necessarily limited resolution since the maximum angle for data collection is limited. Even within these limits there may be missing data because of other experimental difficulties. It is therefore not always possible to be sure that some features of these maps are «real» effects and not artefacts of the missing data.

2.2.2 — The Multipole Expansion

As an alternative to expanding the electron density in its Fourier components is possible to make an expansion in spherical harmonic components about the atomic centres, each harmonic component having an associated radial density function. Such a procedure was first suggested by Kuorki Suonio [8] who showed how to derive the spherical harmonic components directly from the measured structure factors. His technique being based on a Fourier expansion suffers from the same problems as outlined above. An alternative procedure introduced by Stewart [9], [10] and others is to model the spherical harmonic expansion by a limited number of parameters giving the magnitude of the harmonic components and the shape of their associated radial distributions. These parameters are then determined from the observed structure factors by least squares analysis.

The validity of the multipole expansion method rests on the physically reasonable supposition that the valence electron density is associated with the atomic centres and its wave-functions can be well represented by linear combinations of atomic orbitals. It is this supposition that makes it possible to terminate the expansion after relatively few terms leaving the ratio of observations to parameters favourable for least squares refinement. The advantage of the multipole technique is that it gives an analytical expression for the charge density involving relatively few parameters. The multipole representation can then be used to expand the charge density itself or to calculate other properties which depend on it. It must however always be borne in mind that the derivation of any property which implies a higher resolution than that imposed by the limit of data collection has no experimental justification.

2.2.3 — The «free atom» model

Whether a Fourier or a multipole technique is used the charge density represented is usually the difference between a «free atom» model and the observations. Several different bases for the «free atom» model are used by different groups and it is as well to be sure that the same basis has been used for subtraction before comparing results. The two most frequently used models are the true free atom model in which the sum of the neutral free atom form factors is used and the prepared atom model in which the form factors appropriate to the atom or ion in the state nearest to that expected in the solid is used. To take a simple example: for NaCl the free atom model would use the sum of the neutral sodium and chlorine atoms whereas the prepared atom model would use the form factors for Na^+ and Cl^-. Clearly the difference density, often called the deformation density would be completely different in the two cases.

2.2.4 — Fitting the data to a model

Perhaps the most satisfactory method of using the results of a charge density study would be to compare them with a theoretical model which could include a few adjustable parameters to be fitted to the data by least squares. Unfortunately such models are hardly ever available for crystals on which charge density sutdies have been made. There have been some attempts to correlate the parameters obtained in multipole analyses with Mulliken population numbers, but these are of doubtful theoretical validity. It is to be hoped that studies undertaken in the future will cover cases where a fit of theoretical parameters to the experiments is possible.

2.3 — *Objectives of Charge Density Studies*

It has now been clearly demonstrated that it is possible with careful measurements on well chosen materials to measure charge densities with sufficient precision to show effects which are associated with chemical bonding. The question of what use are such charge density maps, may now be asked. The first and most obvious purpose of such studies is to serve as a test for theoretical calculation. For relatively simple molecules, it is now claimed that theoretical wave functions can be calculated to any required degree of accuracy. A proper comparison between theory and experiment is more difficult to obtain mainly because most theoretical calculations pertain to molecules and not to crystals. There are of course many cases where the number of electrons in the molecule is such that self consistent ab-initio calculations would be too costly or time-consuming and recourse is made to more approximate theoretical methods. Here the comparison between theory and experiment can be used to select the most appropriate of several possible approximate methods.

In cases where good theoretical models are not available one may ask whether it is possible to use the results of charge density studies to derive other chemical properties such as electrostatic potentials, dipole and higher moments which can be compared with results obtained using other techniques. Such comparisons usually turn out to be disappointing because of the difficulty of adequately accounting for the very different spatial resolutions associated with the different types of experiment.

The areas where perhaps the most can be expected from the results of charge density measurements are those where theoretical calculations are the most difficult and one may hope that deformation charge densities will help in understanding chemical and physical properties. In many electron systems such as organo metallic compounds or transition metal alloys or compounds there are very few reliable calculations of electron distribution. In the case of metals rather good band structure calculations are sometimes available but as has often been pointed out the spatial properties of the eigenvectors provide a much more rigorous test of the correctness of a theoretical model than do the eigenvalues. In these many-electron systems X-ray scattering determinations become difficult for reasons pointed out at the beginning of this section. On the other hand amongst the transition elements exchange correlation becomes important, resulting in significant numbers of unpaired electrons. For these systems magnetic neutron scattering may be used to probe the distribution of these unpaired electrons. In the final sections of this paper a brief account will be given of the polarized neutron technique for determining unpaired electron density with two examples of its use.

3 — MEASUREMENT OF UNPAIRED ELECTRON DENSITY (SPIN DENSITY)

The magnetic interaction between neutron beam and the unpaired electron density in a crystal offers the possibility of studying the spatial distribution of just those unpaired electrons. This technique, complementary to the X-ray scattering studies avoids a number of the experimental problems outlined in Section 2.1.

3.1 — *Experimental Problems*

3.1.1 — Range of application

In most cases magnetic neutron scattering is by electrons with unpaired spins, and these are just those with energies near to the Fermi energy and therefore involved in solid state interactions and chemical bonding. The core electrons are paired and contribute little if anything to the magnetic scattering. Thus magnetic neutron scattering, where applicable, is sensitive to just those electrons which are of interest to the solid state physicist. The technique can therefore be applied to any magnetic material regardless of atomic number. For example, studies of actinide compounds have shed light on the roles played by 5f and 6d electrons in their magnetism and cohesion.

3.1.2 — Scale Factor

The results of magnetic scattering studies are easily placed on an absolute scale by reference to the neutron nuclear scattering which can be measured under exactly the same experimental conditions.

3.1.3 — Temperature Factors

As for the scale factor, the temperature factors can be determined under the same conditions as the magnetic structure factors. There remains some question as to whether the magnetic electrons will undergo the same thermal vibrations as the atomic nuclei. Up to the present time there is little evidence that any inequality in these factors is sufficiently important to falsify the results.

3.1.4 — Extinction

Extinction is equally important in magnetic scattering studies as in X-ray scattering studies. It may often be more acute since in general larger crystals must be used. If the magnetic scattering occurs as a small perturbation of the nuclear scattering then a reliable correction can be made so long as an empirical expression for the observed intensity in terms of the kinematical intensity can be established (Delapalme et al., [11]). When the magnetic scattering is of the same order of magnitude as the nuclear scattering extinction corrections must be made with care; often observations at a number of different wavelengths are required (Bonnet et al. [12]).

3.1.5 — Multiple Scattering

Multiple scattering can falsify magnetic scattering measurements in just the same way as X-ray scattering measurements, and can be avoided in the same ways.

3.1.6 — Thermal Diffuse Scattering

TDS does not present a problem for magnetic scattering measurements using polarized neutrons which do not require integrated intensity measurements.

3.2 — *Magnetic Neutron Scattering an the Polarized Beam Technique*

3.2.1 — The Magnetic Structure Factor and Magnetic Form Factors

The neutron is scattered in a magnetic material because of the interaction between its magnetic moment and magnetic fields in the material. In just the same way as for X-ray scattering one can define a magnetic structure factor

$$\mathbf{M}\ (\mathbf{k}) = \int_{\text{cell}} \mathbf{M}\ (\mathbf{r})\ e^{i\mathbf{k}.\mathbf{r}}\ d\mathbf{r} \tag{1}$$

where $\mathbf{M}\ (\mathbf{r})$ is the intensity of magnetization or magnetization density in the material. The principal difference from the X-ray or nuclear structure factor is that $\mathbf{M}\ (\mathbf{k})$ being the Fourier transform of a vector is itself a vector. The intensity of scattered neutrons is not directly related to the magnetic structure factor but to its projection on the plane perpendicular to the scattering plane. The generalised magnetic interaction vector is then given by

$$\mathbf{M}_{\perp}(\mathbf{k}) = \hat{\mathbf{k}} \times \mathbf{M}\ (\mathbf{k}) \times \hat{\mathbf{k}} \tag{2}$$

and the cross-section for magnetic elastic scattering of unpolarized neutrons

$$\left(\frac{d\sigma}{d\omega}\right)_{\text{magn. el.}} = |\mathbf{M}_{\perp}(\mathbf{k})|^2 \tag{3}$$

If the magnetization density can be divided amongst well defined atoms or ions then one can define a magnetic form factor for each atom

$$\mathrm{f}(\mathbf{k}) = \left(\int \mathbf{m}\ (\mathbf{r})\ \mathrm{e}^{i\mathbf{k}.\mathbf{r}}\ \mathbf{dr}\right) \Big/ \left(\int \mathbf{m}\ (\mathbf{r})\ \mathbf{dr}\right) \tag{4}$$

where $\mathbf{m}\ (\mathbf{r})$ is the magnetization density associated with the atom. The magnetic structure factor can be written easily in terms of from factors as

$$\mathbf{M}\ (\mathbf{k}) = \sum_{n} \mathrm{f}_n\ (\mathbf{k})\ \mathbf{M}_n\ \mathrm{e}^{i\mathbf{k}.\mathbf{r}_n} \tag{5}$$

Here $\mathrm{f}_n\ (\mathbf{k})$ is the form factor for the nth atom at a distance r_n from the origin and $\mathbf{M}_n$ is the magnetic moment on this atom. The sum is over all atoms in the unit cell.

When the magnetization is due to electrons in a single unfilled shell one may write the form factor as

$$\mathrm{f}(\mathrm{k}) = \sum_{l} \mathrm{A}_l\ (\mathrm{k}) < \mathrm{J}_l\ (|\mathbf{k}|) > \tag{6}$$

where

$$< \mathrm{J}_l\ (|\mathbf{k}|) > = \int_0^\infty \mathrm{U}^2\ (\mathrm{r})\ \mathrm{J}_l\ (\mathrm{kr})\ \mathrm{dr} \tag{7}$$

Here $\mathrm{J}_l\ (\mathrm{kr})$ is the spherical Bessel function of order l and $\mathrm{U}^2\,(\mathrm{r})$ the radial distribution function of electrons in the open shell. The coefficients $\mathrm{A}_l\,(\mathrm{k})$ depend both on the direction of the scattering vector **k** and on the magnetic configuration. For a spherically symmetric spin-only ion such as the Mn^{2+} $3\mathrm{d}^5$ configuration only A_0 is finite. For the general spin-only case with d electrons A_0, A_2 and A_4 can be non-zero. The situatiton is more complicated when some orbital moment is present. The orbital magnetization density at a point is not due to the electrons at that point but to all electrons contributing to current loops closing around the point. An approximation to the spherical form factor valid for small **k** when orbital moment is present is given by the dipole approximation (Marshall and Lovesey [13]) as

$$\mathrm{f}(\mathrm{k}) = 2\ \mathrm{S} < \mathrm{J}_0\ (\mathrm{k}) > + \mathrm{L}\ (< \mathrm{J}_0\ (\mathrm{k}) > + < \mathrm{J}_2\ (\mathrm{k}) >) \tag{8}$$

where S and L represent the spin and orbital angular momenta of the ion. Fig. 1 shows the k dependence of the three integrals $< J_0 >$, $< J_2 >$ and $< J_4 >$ for the Mn^{2+} ion. Also shown for comparison is the total charge X-ray form factor.

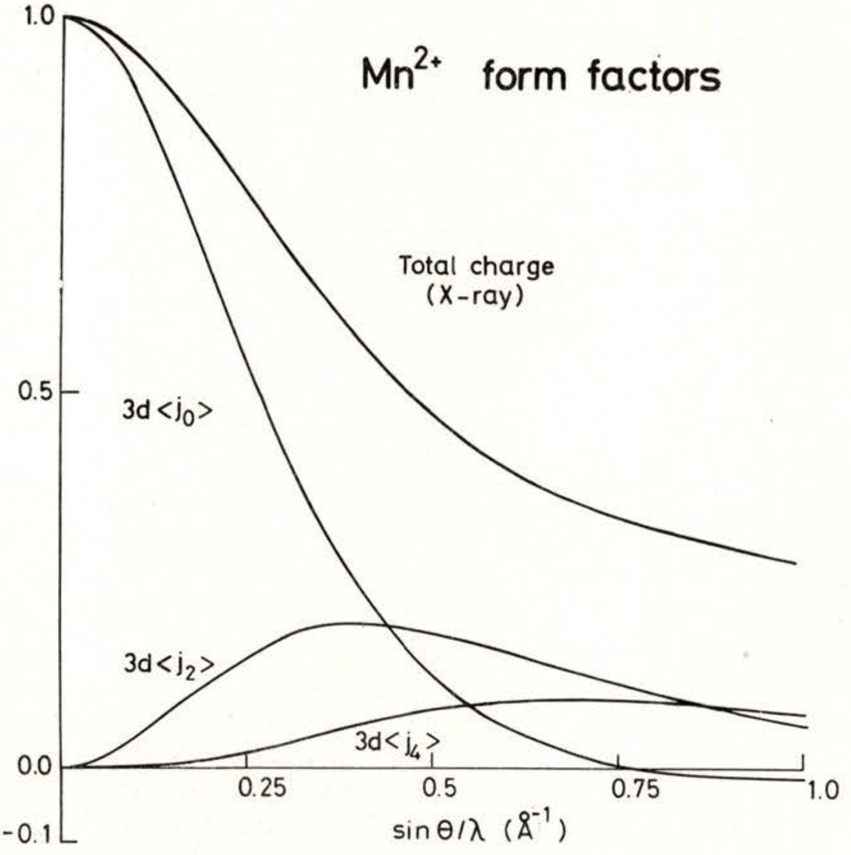

Fig. 1 — The total charge and 3d form factors for the Mn^{2+} ion.

3.2.2 — Scattering of Polarized Neutrons

The cross-section for scattering of polarized neutrons is the sum of two terms, one corresponding to scattering without change of spin state and the other («spin-flip» cross-section) comprises neutrons whose spin was changed by the scattering.

$$\frac{d\sigma}{d\omega}(\uparrow\uparrow) \propto |N(\mathbf{k}) + \hat{\mathbf{u}} \cdot \mathbf{M}_{\perp}(\mathbf{k})|^2 \tag{9}$$

$$\frac{d\sigma}{d\omega}(\uparrow\downarrow) \propto |\hat{\mathbf{u}} \times \mathbf{M}_{\perp}(\mathbf{k})|^2 \tag{10}$$

Here N (**k**) is the neutron-nuclear structure factor and $\hat{\mathbf{u}}$ a unit vector parallel to the neutron polarization. The non-spin flip cross-section is polarization dependent if there is interference between nuclear and magnetic scattering. The flipping ratio which is the ratio between the cross-sections for two opposite neutron spins is

$$R = \frac{|N(\mathbf{k})|^2 + |\mathbf{M}_{\perp}(\mathbf{k})|^2 + N^*(\mathbf{k})\,\hat{\mathbf{u}} \cdot \mathbf{M}_{\perp}(\mathbf{k}) + N(\mathbf{k})\,\hat{\mathbf{u}} \cdot \mathbf{M}^*_{\perp}(\mathbf{k})}{|N(\mathbf{k})|^2 + |\mathbf{M}_{\perp}(\mathbf{k})|^2 - N^*(\mathbf{k})\,\hat{\mathbf{u}} \cdot \mathbf{M}_{\perp}(\mathbf{k}) - N(\mathbf{k})\,\hat{\mathbf{u}} \cdot \mathbf{M}^*_{\perp}(\mathbf{k})} \tag{11}$$

and it is this flipping ratio which is measured in most polarized neutron experiments.

An instrument for making polarized neutron measurements is shown in Fig. 2. A monochromatic polarized beam is produced

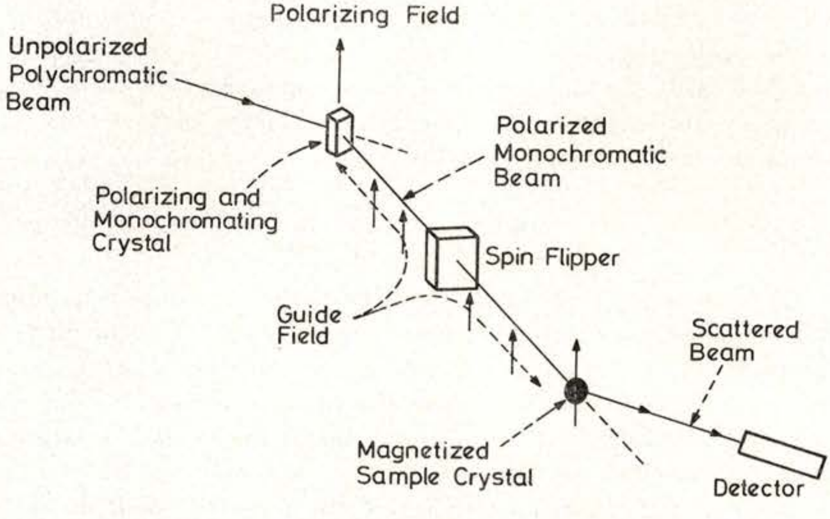

Fig. 2 — Schematic representation of a polarized neutron diffractometer.

by a crystal which has zero cross-section for one spin state. The polarization is retained between polarizer and specimen by magnetic guide fields. At some point in this path a «spin-flipper» is introduced whose function is to reverse the polarization when it is «on» and to leave it unchanged when it is «off». In an experiment the diffractometer and sample are set so that the peak of a Bragg reflection enters the counter and the ratio between the counting rates for the two neutron spin states is determined.

In the simple case that both $\mathrm{N}(\mathbf{k})$ and $\mathbf{M}(\mathbf{k})$ are real (centrosymmetric structures) and the polarization is parallel to the magnetization and perpendicular to $\mathbf{k}$ the flipping ratio R becomes

$$\mathrm{R} = \frac{\mathrm{N}(\mathbf{k})^2 + \mathrm{M}(\mathbf{k})^2 + 2\ \mathrm{N}(\mathbf{k})\,\mathrm{M}(\mathbf{k})}{\mathrm{N}(\mathbf{k})^2 + \mathrm{M}(\mathbf{k})^2 - 2\ \mathrm{N}(\mathbf{k})\,\mathrm{M}(\mathbf{k})} = \left(\frac{1+\gamma}{1-\gamma}\right)^2 \qquad (12)$$

where $\gamma = \mathrm{M}(\mathbf{k}) / \mathrm{N}(\mathbf{k})$.

In general R can only differ from unity if there is magnetic and nuclear scattering in the same reflection. This condition is satisfied if any part of the magnetization has the same periodicity as the nuclear structure as is the case in a ferromagnet or in a paramagnet in an applied field. It is not satisfied by antiferromagnetic structures in which the magnetic cell is some multiple of the nuclear one.

The ratio γ is obtained from the flipping ratio R by solving the quadratic equation (12). The result assuming perfect polarization and complete spin reversal is

$$\gamma = (\mathrm{R} + 1 \pm \sqrt{4\mathrm{R}}) \,/\, (\mathrm{R} - 1) \qquad (13)$$

The choice of root depends on whether the absolute magnitude of the magnetic scattering is greater or less than that of the nuclear scattering. There is no uncertainty in the sign of γ which shows that the polarized neutron technique determines the sign of the magnetic scattering with respect to that of the nuclear scattering in centrosymmetric structures.

One of the major advantages of the polarized neutron technique is that integrated intensities are not needed — it is just the ratio between peak counting ratios for the two spin states that is measured and this ratio can be obtained with high accuracy. In most cases magnetic neutron scattering is much weaker than nuclear scattering and $|\gamma|$ is significantly less than one. For small γ (13) can be simplified to

$$R = 1 + 4\gamma \tag{14}$$

The sensitivity of the polarized neutron technique is demonstrated by comparing (14) with the fraction of the integrated intensity due to magnetic scattering

$$\Delta I / I = 1 + \gamma^2 \tag{15}$$

The technique can be used to measure extremely small γ since down to 0.1 % accuracy or better there is little except the counting statistics to limit the accuracy with which R can be measured. Measurements of very small γ values do however require long counting times and high incident intensity. To give some idea of the orders of magnitude involved the counting rate at a high flux reactor from a strong reflection of a simple crystal will probably not much exceed 10^4 cps, which implies measurement times from a few minutes to several days.

To illustrate the use of the technique the last two sections of this paper will be used to describe two recent studies carried out at the Institute Laue-Langevin, one showing the measurement of a very small magnetic moment in a paramagnetic metal (Rhadhakrishna and Brown [14]) and the other demonstrating how covalent bonding affects the magnetic form factor in an ionic compound (Brown, Ziebeck and Radhakrishna [15]).

4 — THE PARAMAGNETIC FORM FACTOR OF TECHNETIUM

Technetium, which is the 4d analogue of manganese in the 3d and rhenium in the 5d transition series, does not occur naturally. It can be obtained as the radioactive isotope ^{99}Tc, a soft β-emitter with a half life of 5×10^5 years. Technetium is a hexagonal close-packed metal, it has a paramagnetic susceptibility which remains essentially constant at 10^{-6} emu/g over the temperature range 80-1400 K. The form factor of technetium is of interest because of the rather strange from factors found for other hexagonal close-packed metals (Moon et al. [16]) such as scandium, yttrium and titanium which indicate considerable delocalisation of the magnetic electrons.

An applied field of 4.8 T induces an aligned moment of 0.94 ± 10^{3} μ_B per atom of technetium and the expected γ value at the lowest angle reflection is aout 2×10^{-4} showing that measurement of the paramagnetic magnetization density is at the lower limit of possibility. However, large single crystals of technetium have been grown by Kostorz and Michailovitch [17] and two were lent to us by the Oak Ridge National Laboratory. These crystals gave counting rates greater than 10^{5}/s and the rate used was limited by the detector dead time. In about 28 days measuring time we were able to determine the flipping ratios of the eight lowest angle reflections with an accuracy of around one part in 10^{4}. At this level of precision in flipping ratio measurements account must be taken of small systematic errors implicit in the measurement technique. Moon et al. [18] discuss some of these errors which are most troublesome if the crystal rocking curve is narrow or the crystal slightly mis-set. In the case of technetium the rocking curves were quite broad (0.25° f. whm) and an on-line maximisation option in the diffractometer control package was used to ensure that the crystal was set to the centre of the reflection for each measurement. The precision of the flipping ratios was estimated from the degree of reproducibility between repeated measurements of all available equivalent reflections; in no case was the reproducibility found to be significantly different from that expected from the counting statistics.

Several different physical effects must be taken into account before the paramagnetic structure factors can be obtained from the flipping ratios, the most important of these are extinction, diamagnetism and Schwinger scattering. To determine the degree of extinction a separate experiment was carried out using unpolarized neutrons. The integrated intensities of reflections were measured at three different wavelengths in zero field; the results showed the effect of extinction on the flipping ratios to be negligible. Calculation of the diamagnetic scattering and Schwinger scattering showed them to be of the same order of magnitude as the experimental errors. Once corrected for these effects the resultant magnetic structure amplitudes are the Fourier components of the paramagnetic magnetization density. They are converted to points on the paramagnetic form factor by dividing by the geometric structure factors and the value of the bulk magnetization per cell. The bulk magnetization must also be corrected for the diamagnetic moment. The results are shown in Fig. 3; they fall on a

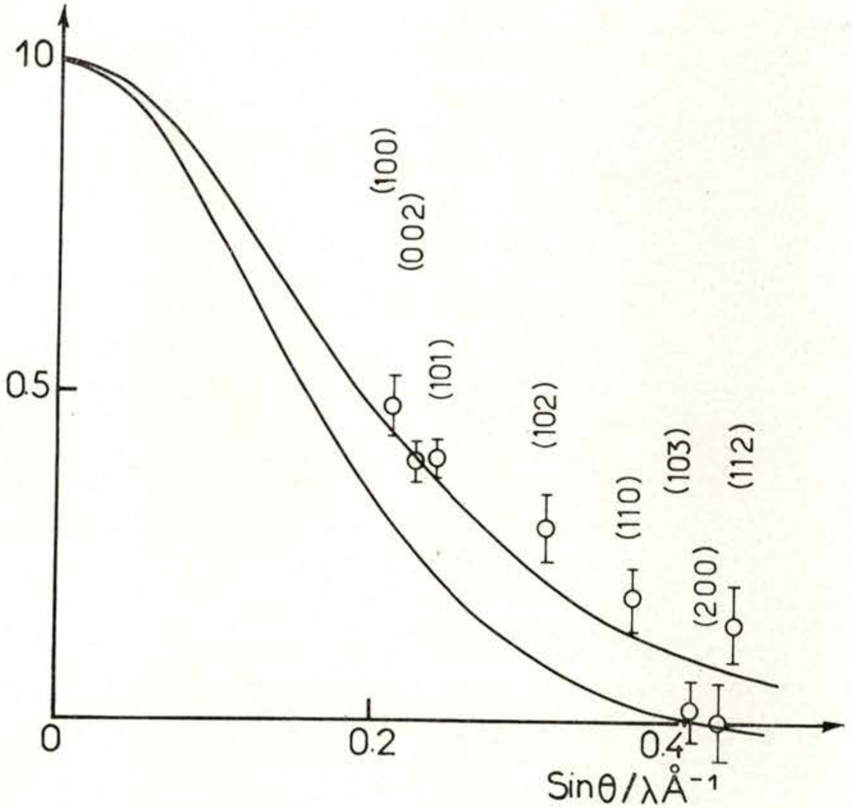

Fig. 3 — The paramagnetic form factor of technetium. The experimental points with their estimated errors are shown. The lower full curve corresponds to the spin-only form factor for Tc 4d electrons. The upper full curve is the form factor in the dipole approximation with 70 % orbital moment.

reasonably smooth curve unlike those for scandium, yttrium and titanium. This confirms that the behaviour of these latter elements is due to their early positions in the transition series rather than to their hexagonal structures. The experimental points lie well above the lower full curve of figure 3 which represents the spin-only form factor for Tc 4d electrons. This is not unexpected since a temperature independent susceptibility may have a large Van-Vleck orbital component. The experimental data have been fitted to a Tc 4d form factor in the dipole approximation (equation (8)) allowing the ratio of spin to orbital moment to vary. The result suggests that 70 % of the moment is orbital, and the resultant form factor is shown in the upper solid curve of figure 3. This model gives a reasonably good account of the experimental data; further refinement must await a good calculation of the technetium band structure. This study of technetium is an example of the measurement of a very small magnetization in a very simple structure. The results will provide a stringent test of any band structure calculation.

5 — COVALENT EFFECTS IN THE MAGNETIZATION DENSITIES OF $CrCl_3$ AND $CrBr_3$

Magnetization measurements on chromium tri-bromide and chromium tri-chloride show that at 4.2 K fields of some 0.3 T are sufficient to produce essentially parallel alignment of all the chromium moments. Under these conditions the polarized neutron scattering technique can be used to study their magnetization density distributions. Both $CrCl_3$ and $CrBr_3$ have the rhombhedral $FeCl_3$ structure at low temperatures, the chromium ions are octahedrally co-ordinated by halide ligands and the octahedra share three of their twelve edges to form sheets which lie perpendicular to the triad axis. Single crystals of both compounds were grown for us at the M. P. I. Stuttgart. They were mounted with a $< 01.0 >$ axis parallel to the difractometer ω axis which is the magnetization and polarization direction. The flipping ratios of all reflections in the zero, first and second layers were measured at 4.2 K in an applied field of 1.4 T. The $\sin\theta/\lambda$ limit was 0.5 for $CrCl_3$ and 0.75 for

$CrBr_3$. Integrated intensities measured in a separate experiment with unpolarized neutrons were used to determine the structural parameters and temperature factors at 4.2 K.

Magnetic structure factors were obtained from the observed flipping ratios using the structural parameters at 4.2 K to give the nuclear structure factors. The magnetic structure factors can be displayed as a form factor by dividing through by the chromium geometric structure factors. The form factors so obtained were compared with a theoretical Cr^{3+} free ion 3d form factor. In both compounds the experimental curve drops much more sharply at low angles but the outer parts of both experimental and theoretical curves have rather closely the same shape. In $CrBr_3$ where the measurements extend to $\sin\theta/\lambda = 0.75$ experimental and theoretical curves drop to zero at about the same angle.

The difference in shape between the experimental and theoretical free ion form factors is not unexpected since covalency in these compounds should be significant. For a ferromagnetically aligned material the delocalisation associated with transferred spin should lead to a narrower form factor. To quantify this effect the magnitude of the 3d-like part of the scatterring has been estimated by fitting the moment value of a Cr^{3+} spherical 3d form factor to those data with $\sin\theta/\lambda > 0.25$. Reasonable fits were obtained with $\mu_{3d} = 2.46(4)$ for $CrBr_3$ and 2.24(6) for $CrCl_3$. Magnetization and resonance measurements on chromic salts suggest that the 3d electrons in $CrCl_3$ and $CrBr_3$ should be described by the orbital singlet $^4\Gamma_2$ obtained as ground state from a ^4F term under an octahedral field. The scattering from this state is not isotropic and the calculated anisotropy of its form factor reproduces rather well the anisotropy of the observations as may be seen from Fig. 4. In a simple model including covalent effects, the magnetization density can be split into a 3d part, a ligand part and an overlap part, this latter being negative for antibonding orbitals. Hence the magnetisation density may be written

$$\rho(\mathrm{r}) = \mathrm{N}(\rho_{3d}(\mathrm{r}) + \mathrm{A}^2 \rho_{\mathrm{ligand}}(\mathrm{r}) - \mathrm{A}\,\rho_{\mathrm{overlap}}(\mathrm{r}))$$

N is a normalising constant obtained by integrating the density over a unit cell so that $N = (1 + 3A^2 - 3AS)^{-1}$ where S is the value of the overlap integral. Since the observed 3d moment is reduced in $CrCl_3$ and $CrBr_3$, N must be less than unity and hence $A > S$. A lower limit of $A^2 > 0.04$ is given if S is very small. A preliminary investigation of the delocalised moment has been made using Fourier techniques. These give some evidence for magnetic density transferred towards ligand sites but the most significant feature of the maps is an accumulation of density

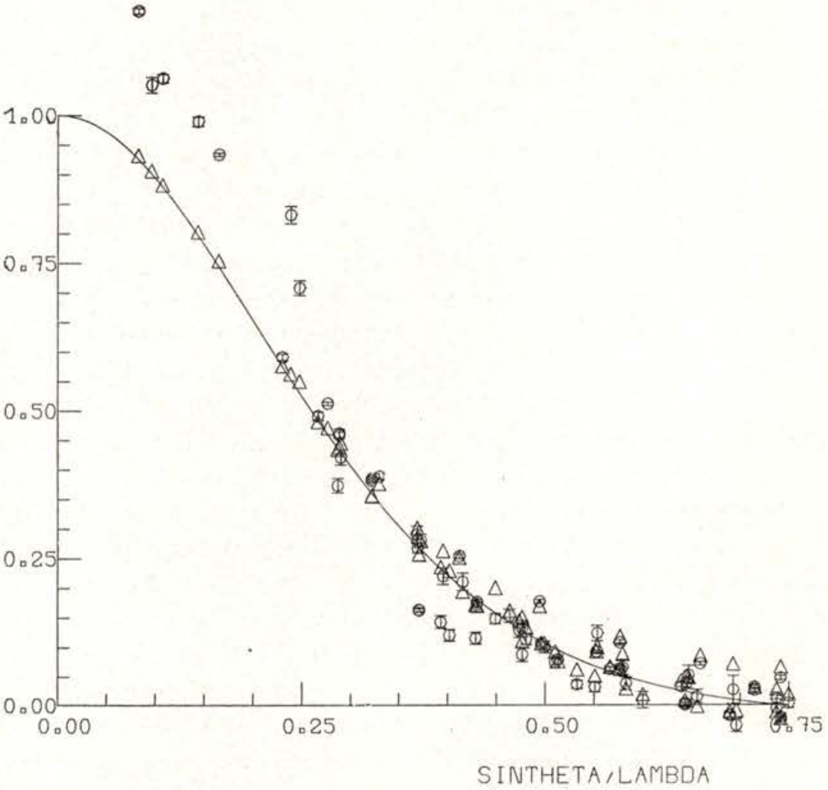

Fig. 4 — The form factor derived from h0l reflections in $CrBr_3$: circles mark observed values with their error bars and the triangles correspond to the calculation for Cr^{3+} $^4\Gamma_2$. The full curve is the spherical 3d form factor for a Cr^{3+} free ion.

between near neighbour chromium ions within the chromium layer as can be seen in Fig. 5. This density demonstrates the importance of the shared edges of the octahedron of halide ions in the description of covalent interactions in these compounds.

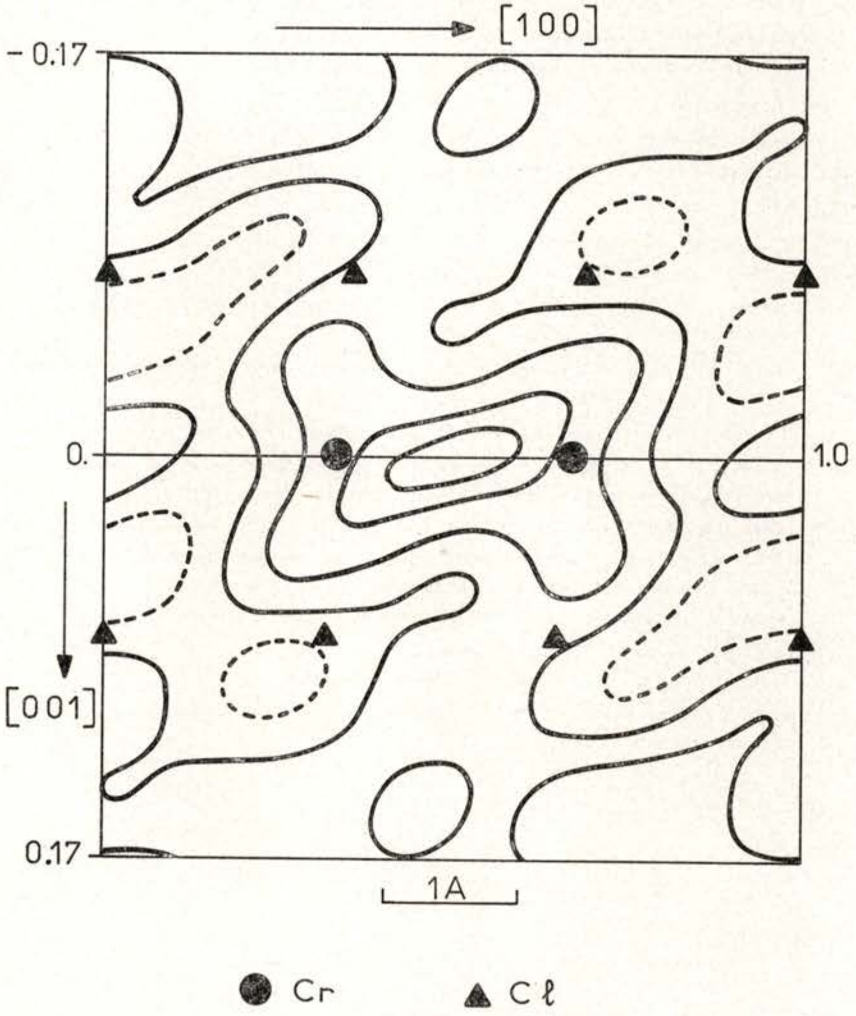

Fig. 5 — Fourier projection of the delocalised spin density in $CrCl_3$ on the (10.1) plane. The projected positions of Cr^{3+} and Cl^- ions are shown. The contour interval is 0.05 $\mu_B/\text{Å}^2$; negative contours are shown as dashed lines.

REFERENCES

[1] COPPENS, P., *Science*, **158**, 1577 (1967).

[2] BECKER, P. and COPPENS, P., *Acta Cryst.*, **A30**, 129 (1974).

[3] BECKER, P. and COPPENS, P., *Acta Cryst.*, **A31**, 417 (1975).

[4] THORNLEY, F. R. and NELMES, R. J., *Acta Cryst.*, **A30**, 748 (1974).

[5] COOPER, M. J. and ROUSE, K. D., *Acta Cryst.*, **A24**, 405 (1968).

[6] ROUSE, K. D. and COOPER, M. J., *Acta Cryst.*, **A25**, 615 (1969).

[7] COCHRAN, W., *Acta Cryst.*, **A25**, 95 (1969).

[8] KURKI SUONIO, K., *Report Series in Physics* 3/69, University of Helsinki.

[9] STEWART, R. F., *J. Chem. Phys.*, **58**, 1668 (1973).

[10] STEWART, R. F., *Acta Cryst.*, **A32**, 565 (1976).

[11] DELAPALME, A., LANDER, G. H. and BROWN, P. J., *J. Phys.*, **C11**, 1441 (1978).

[12] BONNET, M., DELAPALME, A., BECKER, P. and FUESS, H., *Acta Cryst.*, **A32**, 945 (1976).

[13] MARSHALL, W. and LOVESEY, S. W., *Theory of thermal neutron scattering*, p. 156, O.U.P. (1971).

[14] RADHAKRISHNA, P. and BROWN, P. J., *J. Phys.*, **F10**, 489 (1980).

[15] BROWN, P. J., ZIEBECK, K. R. A. and RADHAKRISHNA, P., *Argonne Conference on Neutron Scattering* Aug. 1981 (In press).

[16] MOON, R. M., KOEHLER, W. C. and CABLE, J. N., *Proceedings of the Conference on Neutron Scattering*, Gatlinburg Tennessee p. 577 (CONF-760-601-P2) National Technical Information Service US Department of Commerce, Springfield Virginia.

[17] KOSTORZ, G. and MICHAELOVITCH, S., in *Proc. 12th Int. Conf. on Low Temp. Phys.* p. 341, Academic Press of Japan (1970).

[18] MOON, R. M., KOEHLER, W. C. and SHULL, C. G., *Nucl. Instrum. Meth.*, **129**, 515 (1975).