Spin Density and Bonding in the $CoCl_4^{2-}$ Ion in Cs_3CoCl_5. Part 1. Magnetic Structure Factors from Polarised Neutron Diffraction

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The magnetic structure factors of 101 unique *hkl* reflections of Cs_3CoCl_5 have been measured at 4.2 K with a magnetic field of 4.6 T along the crystal *c* axis. A further 110 unique reflections with a magnetic field of 1.5 T along the *a* axis have also been obtained. A statistical analysis of the errors in the data sets has been made so that the reliability of their interpretation in models of chemical interest may be assessed. Ten of the *c*-data reflections, all based on low nuclear structure factors, were rejected on statistical grounds. The major sources of error in the data were found to be extinction and multiple scattering, with counting statistics and machine instability playing a lesser role. The two data sets agree well, no reflection exceeding 3σ from its scaled value. Using a free-ion Co^{2+} magnetic form factor, the data are reproduced to within 5% by a single spherical model of spin occupation $3d^{2.4}\,x^{0.6}$, where *x* represents orbitals much more diffuse than Co^{2+} 3*d* functions. That is, the data indicate that *ca.* 80% of the spin is located in Co^{2+} 3*d*-like orbitals and 20% is in more diffuse orbitals, whether cobalt-centred or delocalised onto the chlorine ligand atoms. Covalence is indicated by the non-zero intensities of the *l*-odd data. Small, but statistically significant deviations from the above model are expected to be correlated with, for example, the concentration of the Co^{2+} 3*d* spin into the t_2 orbitals and the details of the distribution of the diffuse '*x*' population.

An understanding of the bonding in transition-metal complexes requires an accurate knowledge of slight changes from free-atom wavefunctions for some or all of the atoms in the complex. The effects of these changes are made quite obvious by many experimental techniques. Polarised neutron diffraction is the only one which simultaneously is sensitive to details in the wavefunction and yields sufficient observables to realistically model it. Only in diffraction techniques is there a *direct* relationship between the observations and the wavefunction.[1,2] The polarised neutron diffraction experiment measures the Fourier components of the magnetisation distribution in the crystal. As well as the spin, the magnetisation includes a 'nuisance' contribution from any orbital-angular momentum present. Unlike *X*-ray diffraction, the polarised neutron diffraction experiment is not dominated by the contributions from the chemically uninteresting core electrons.

Following the pioneering work on MnF_2,[3] and on $Mn[CO_3]$,[4] Wedgwood [5] performed polarised neutron diffraction experiments on single crystals of $K_2Na[CrF_6]$. Although his results clearly show the t_{2g} *d*-electron spin distribution around the chromium nucleus expected for a d^3 ion in an environment of octahedral symmetry, it is less clear that they are accurate enough to quantitatively describe the effects of covalency, which are expected to be small anyway. We have initiated a program to study the spin-density distribution in a number of more covalent compounds [6] with improved experimental accuracy and have chosen a substance with a higher 4.2 K magnetisation at accessible magnetic field strengths. A further consideration was to choose a compound of crystal symmetry in which some of the reflections show intensity due only to covalence, the *d*-orbital spin density providing *no* contribution. For these reasons Cs_3CoCl_5 is the subject of the present studies.

The compound Cs_3CoCl_5 crystallises in a tetragonal space group ($I4/mcm$) in which layers of $2Cs^+$ and Cl^- ions interleave with layers of Cs^+ and $CoCl_4^{2-}$ ions.[7-10] The site symmetry of the $CoCl_4^{2-}$ ion in the compound is D_{2d} ($\bar{4}2m$), and it is only slightly distorted from tetrahedral symmetry (T_d). In a tetrahedral environment the d^7 Co^{2+} ion, in the crystal-field model, adopts a configuration $e^4t_2^3$ with the orbitally non-degenerate ground term $^4A_2$. The magnetic susceptibility is anisotropic with χ_c greater than χ_a.[11,12] The maximum moment, $\langle\mu\rangle$, accessible to use in this substance reaches 3.6 B.M.† per ion compared with 1.08 B.M. per ion in $K_2Na[CrF_6]$.

The Co–Cl bond is expected to be appreciably more covalent than the Cr–F bond. This covalence gives magnetic intensity in *l*-odd reflections of Cs_3CoCl_5, because of the non-centrosymmetric nature of this T_d complex, whereas the centrosymmetric metal 3*d* orbitals give *no* intensity in these reflections. The *l*-even reflections contain both contributions.

Because of its high symmetry and simple chemical structure Cs_3CoCl_5 has been studied by a wide variety of physical techniques apart from the structural studies [7-10] mentioned above. The magnetic susceptibility, anisotropy, and magnetisation have been thoroughly studied at low temperatures.[11-13] There are data on the electron spin resonance,[12] specific heat,[14] optical and Raman spectra,[15,16] and the infrared spectra.[16,17] The $CoCl_4^{2-}$ ion is sufficiently small that an *ab initio* molecular-orbital calculation has been performed at a double-zeta level of basis set.[18]

In this paper we describe the collection of two polarised

† Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

neutron diffraction data sets on Cs_3CoCl_5, analysis of their concordance and the experimental errors, and the qualitative features of the data. The subsequent paper [19] uses simple modelling of the spin density in a way suggested by elementary quantum mechanics and discusses the physical significance of the parameters extracted. A different method of fitting the data, based on the multipole method, providing an empirical description and illuminating the amount of significant information in the data, will be published elsewhere.[20]

EXPERIMENTAL

Large deep blue crystals of Cs_3CoCl_5 were grown by slow evaporation of an aqueous solution of $CoCl_2 \cdot 6H_2O$ containing an excess of CsCl. The tetragonal crystals were of regular habit with {001} and {110} well developed, and {112} just visible. The crystal employed in this experiment was the same one that was used in the previous 4.2 K nuclear structural analysis [9] and measured 3.16 × 3.04 × 1.67 mm, the smallest dimension being normal to {001}. The crystal was cooled quickly to prevent any possible phase change.[21]

The spin-flip ratios of a number of reflections were measured in two experiments with different crystal orientations using the D3 polarised neutron diffractometer at the High-Flux reactor of the Institut Laue-Langevin, Grenoble. This machine has normal-beam geometry.

Firstly, the crystal was aligned with its *a* axis parallel to a magnetic field of 1.49 T at a temperature of 4.2 K (*a* data). Individual Bragg-peak flipping ratios were obtained by centering the peak using an ω-search, and counting for *ca.* 30 min using the peak/background/flipping times, determined by the D3 software, which optimise the observed flipping ratio accuracy. The incident neutron wavelength was 99.3 pm with beam polarisation 0.961 0 ± 0.000 3 and flipper efficiency 1.000 0 ± 0.000 3. A restriction on the height of the lifting counter above the horizontal plane (ν axis), imposed by the magnet windings, limited observations to $0 \leqslant h \leqslant 4$. Usually four or more of the eight equivalences accessible for a general (*hkl*) reflection were measured, with repetition sometimes to improve the counting statistics. 718 Measurements were made on 497 equivalences of 168 unique reflections. The data represent a complete set out to (sin θ)/λ 3.9 nm^{-1}, with more data out to (sin θ)/λ 7.3 nm^{-1}. The major bias in the data is the lack of reflections with $h \approx k > 4$ imposed by the physical limitation on the ν axis. The flipping ratios for *l*-odd reflections were not significantly different from unity, and were removed from further analysis leaving 110 unique reflections. The second experiment was made with the crystal aligned with its *c* axis parallel to a magnetic field of 4.6 T at a temperature of 4.2 K (*c* data). The incident neutron wavelength was 90.02 pm and the beam polarisation factor was 0.973 3 ± 0.000 3. Spin-flip ratios were measured in the same way as previously. The ν-axis limitation this time restricted data to $0 \leqslant l \leqslant 5$. As a result of our analysis of the previous data only a few Bragg reflections with structure factors less than 0.025 pm per unit cell were measured. All accessible equivalents of all remaining accessible unique reflections were measured, many times, out to a (sinθ)/λ of *ca.* 7.0 nm^{-1}, beyond which the observed flipping ratios became obscured by counting statistics, due to the decay in the magnetic form factor with wave-vector. 650 Measurements were made on 476 equivalences of 101 unique reflections. The major difference from a complete sphere of data is the lack of any data in the set with $l \geqslant 6$. It will be seen that this bias complements that of the previous set to produce a fairly complete set of data with (sinθ)/λ < 7.0 nm^{-1}. In this case the larger magnetisation than for the *a* data allowed significant flipping ratios to be collected for the *l*-odd reflections. Since these reflections contain information about covalence undiluted with *d*-electron information, they were counted for significantly longer times, in total, than were the *l*-even data.

ANALYSIS OF THE RESULTS

To provide a basis for modelling, the data must be reduced to a set of magnetic structure factors $F_M(hkl)$, (F_M), which are unbiased, and whose errors $\sigma_M(hkl)$ are estimated in a meaningful way. The effect of such factors as extinction, multiple scattering, and instrumental stability must be estimated if the goodness-of-fit, χ^2, of the model is to be believed. Such an estimate arises firstly from a consideration of the self-consistency of the individual measurements of a unique reflection; secondly from the consistency of the errors within a data set; thirdly from the consistency between the different data sets; and lastly, during the process of modelling, by the introduction of parameters (such as extinction).

(*a*) *Comparison of Equivalent Reflections.*—Apart from the small corrections due to polarisation and flipping efficiencies we have observations of the flipping ratio, $R(hkl)$, and the error in it due to counting statistics [see equation (1)] where $I\uparrow_{(hkl)}$ and $I\downarrow_{(hkl)}$ are the

$$R(hkl) = I\uparrow_{(hkl)}/I\downarrow_{(hkl)} = (F_N^2 + 2s^2F_NF_M + s^2F_M^2)/(F_N^2 - 2s^2F_NF_M + s^2F_M^2) \quad (1)$$

respective diffracted intensities from incident neutrons of spin parallel or antiparallel to the applied magnetic field, $F_N(hkl)$ is the nuclear structure factor, and *s* is the sine of the angle between the scattering vector and the direction of magnetisation of the crystal. The value γ defined by equation (2) is the most pertinent quantity

$$\gamma(hkl) = F_M(hkl)/F_N(hkl) \quad (2)$$

for the analysis of the data, and is obtained from the flipping ratios by the solution of a quadratic equation. The appropriate, physically realistic solution for γ must be chosen on the basis of our expectation of the magnetisation density, in this case 3*d*-like. The individual measurements were examined before they were combined to form a best estimate of $\bar{\gamma}$ from a set of equivalent reflections. Some observations were rejected because the observed intensities, $I\uparrow$ or $I\downarrow$, fell well away from those observed in other equivalent reflections or because the ω-axis scan appeared unusual, presumably due to errors in diffractometer setting. This left 718 *a*-data and 650 *c*-data observations. We rejected a reflection if, providing that there were at least four different equivalents originally measured, the deviation of its value ($\gamma - \bar{\gamma}$) from the weighted mean ($\bar{\gamma}$) of all the other

equivalent measurements is more than three times the standard deviation of these other equivalent measurements [$\sigma(\bar{\gamma})$]. This criterion caused *ca.* 10 reflections in the *c*-data set to be rejected. A similar criterion based on kurtosis rather than skewness caused no further reflections to be rejected.

We find from repeated measurements of a standard flipping ratio, $R(110)$, throughout the experiment that errors arising from machine instability are negligible compared with those from counting statistics. If the counting statistical error is small compared with systematic errors between equivalences, then one should use an unweighted mean, and *vice-versa*. To investigate the relative sizes of these errors we have computed a number, n, for each unique reflection set defined by equation (3)

$$n = \sqrt{\frac{N-1}{2}}\left[\frac{\sigma^2(\bar{\gamma})}{N}\sum_1^N \frac{1}{\sigma^2(\gamma)} - 1\right] \qquad (3)$$

where there are N equivalents measured whose variance in $\bar{\gamma}$ is $\sigma^2(\bar{\gamma})$, and each measurement of an equivalent has a counting variance of $\sigma^2(\gamma)$. If the observed variance $\sigma(\bar{\gamma})$ is entirely due to counting statistics, we may expect the frequency distribution of n to be a normal curve. A value $|n| > 3$, then, is strong evidence that systematic errors play an important role in the observed variance. The values of n are given in Supplementary Publication No. SUP 22859 (10 pp.),* together with (hkl), F_N, F_M, and $\sigma(F_M)$ values. Phased F_M values are obtained from γ [equation (2)] using values of F_N calculated from the 4.2 K nuclear structure refinement [9] without regard to extinction. Some reflections are affected by systematic error, but the great majority, including all the *l*-odd reflections, do not seem to be. We have therefore used the weighted mean in estimating $\bar{\gamma}(hkl)$ and its variance. Since we measured each equivalent in a similar way, the counting statistics for each are similar. The difference between weighted and unweighted means is therefore much less than the standard deviation of $\bar{\gamma}(hkl)$. Any large difference would indicate some gross systematic error.

(*b*) *Comparison of Errors within a Data Set.*—For the *c*-data set the crystal habit and alignment give path lengths for the beam in the crystal which were approximately equal for all equivalent reflections. Since counting errors vary only slightly within an equivalent set, then a large value of n, equivalent to a large anisotropy in γ, must reflect a systematic error that can vary quickly with small angular changes in crystal orientation. Such an effect is multiple scattering. If multiple scattering is the cause then we expect n to be large both for low-intensity reflections and for data at low 2θ values; [22-24] we observe $|n| > 4$ only if $\theta < 18°$. Extinction is not a good explanation of the systematic errors since $|n|$ is independent of $F_N^2/\sin(2\theta)$. The *a*-data set contains fewer estimates of $|n|$, due to insufficient equivalences having been measured, but it shows a similar pattern. This implies that differences in multiple scattering between equivalences provide a reasonable explanation of the extra variance in γ over and above that expected from counting statistics. For the *c* data, for $\theta > 20°$ the values of n follow a normal distribution with a standard deviation of 1.1, which is close enough to unity for us to assert that the counting statistics and extinction are by far the dominant errors in that part of the data.

(*c*) *Comparison between the Two Data Sets.*—Since the crystal we have used is markedly tabular, systematic errors dependent on path length, such as multiple scattering and extinction, will differ in the two data sets. The two sets were also measured at different wavelengths. For the normal-beam geometry, with small detector tilt angle ν, the average path length of the neutrons through the crystal in the *c* data will be about double for the *a*-data set. Therefore a comparison between the normalised magnetic form factors $f_a(hkl)$ and $f_c(hkl)$ may reveal some systematic errors. They should be equal in this system where we believe the ground states from which we are scattering are the same in the two experiments (see Part 2).[19] To compare the two sets we need to know the bulk magnetisations under the two experimental conditions, for use as scaling factors, together with any differences in average beam depolarisation factors, $\bar{D}_a(hkl)$ and $\bar{D}_c(hkl)$.

Use of the g factors and ground-state zero-field splitting,[12] $g_\perp = 2.30$, $g_\parallel = 2.40$, $D = -4.30$ cm^{-1}, enables us to calculate the magnetic moments, $F_M(000)$, as $\langle\mu_a\rangle = 2.56$ B.M. per unit cell at $H = 1.49$ T, $T = 4.2$ K and $\langle\mu_c\rangle = 14.5$ B.M. per unit cell at $H = 4.6$ T, $T = 4.2$ K. These values are, respectively, within 1% of the observed value at the relevant temperature and field strength and within 1% of the saturation moment observed at lower temperatures.

The correction for the orbital component of the magnetisation, which differs in the two sets, while small is not negligible for this orbitally non-degenerate $^4A_2$ ground state of Co^{2+}, and arises from spin-orbit coupling of higher states. The corrections to $f_a(hkl)$ and $f_c(hkl)$ can be made using the dipole approximation.[25]

In Figure 1 we have plotted $f_a(hkl)/f_c(hkl)$, for all the reflections in common between the two data sets, against $F_N^2/\sin(2\theta)$. Reflections with low intensity [$F_N^2/\sin(2\theta) < 150$, $F_N < 10$ B.M. per cell] possess a systematic error depressing (f_a/f_c) as F_N tends to zero. We can ascribe this to multiple scattering. This will introduce an intensity into the flipping ratio which is less dependent on neutron spin than F_M, causing R to tend to unity. For low-intensity nuclear reflections with $\gamma > 1$ this will increase the apparent value of F_M. Since path lengths are on average longer in the *c* data than in the *a* data, this effect will depress the ratio (f_a/f_c). The lower that F_N^2 is relative to the multiply scattered intensity, the more important will be the effect. One can provide a very crude estimate if we note that in the nuclear refinement data [9] the observed intensity (F_o^2) is greater than that calculated (F_c^2) for 25 of the 27 reflections with $F_N < 10$ B.M. per cell. If

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

we estimate the multiply scattered intensity as proportional to $(F_o^2 - F_c^2)$, we can write (for equatorial reflections) equation (4) where I_{MS} is the multiply

$$R = (I\uparrow + I_{MS})/(I\downarrow + I_{MS}) = [(F_N + F_M)^2 + (F_o^2 - F_c^2)]/[(F_N - F_M)^2 + (F_o^2 - F_c^2)] \quad (4)$$

scattered intensity. We further assume that the path length in the *c* data is *ca.* 0.4 mm, and *ca.* 0.2 mm in both the *a* data and the structural data. Then, if the multiple scattering is small enough to increase linearly with path length, we may correct (f_a/f_c) for multiple

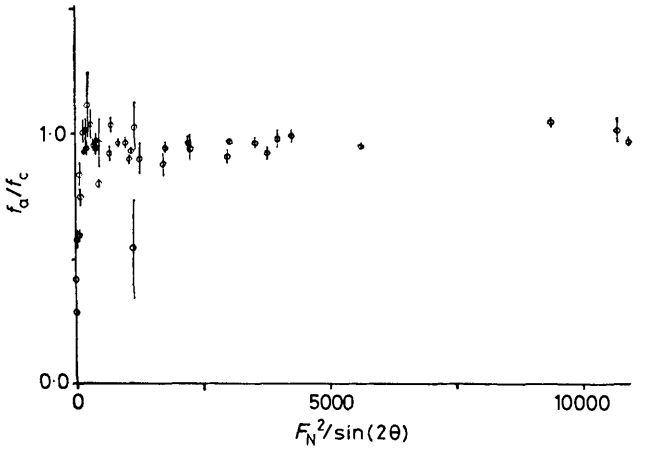

FIGURE 1 Comparison between the two data sets; $\delta f_a(hkl)/f_c(hkl)$ against $F_N^2/\sin(2\theta)$

scattering. For example, for the (422) reflection this raises the ratio from 0.43 to 0.81. While this ' method of correction ' is far too crude to use quantitatively, it shows that the effect of multiple scattering is of the same size and direction as the effect which we observe. Therefore, all *l*-even data with $F_N < 10$ B.M. have not been used as they may be seriously affected by multiple scattering. The *l*-odd data have been retained [except the (411) reflection] as they seem to be less affected by multiple scattering in the nuclear structure-factor experiment.[9] This may be because, for symmetry reasons, F_N^2 for *l* odd is less than for *l* even, making multiple scattering less important.

In Figure 1 the data at higher $F_N^2/\sin(2\theta)$ appear to show no effect of extinction. For small γ, using a Zachariasen-type formula,[26] it was shown [27] that the effect of extinction is to reduce the observed γ value by a factor of $(1 + y^2)/2$, *y* being the ratio of the intensity in the observed Bragg peak to that expected in an identical extinction-free sample. The value of the extinction parameter, *G*, previously measured on the same crystal as $3.3(1) \times 10^2$,[9] implies that there is some extinction present. We assume that *G* has been relatively unaffected by the thermal changes the crystal has undergone in successive experiments. The concordance of the *a* and *c* data is surprising therefore, it being unlikely that the longer path lengths in the *c* data have been compensated by the decrease in wavelength (99.3 to 90.0 pm), together perhaps with a slight decrease in *G*. A more likely explanation is that the extra extinction in the *c* data has been balanced by the greater beam depolarisation in the *a* data. Part 2 in this series deduces a value of 0.91 for $\bar{D}(hkl)$ for *a* and 0.94 for *c*.[19] If we exclude six reflections seriously affected by multiple scattering, the remainder give a mean $(\overline{f_a/f_c})$ of 0.974 ± 0.05. The mean value is not significantly different from 1.00, indicating that the two data sets are indeed compatible. No individual reflection is more than $3\sigma(\overline{f_a/f_c})$ from this value.

(*d*) *Overall Quality of the Data.*—Observed magnetic structure factors are listed in SUP 22859. Those reflections rejected on the grounds of multiple scattering are starred. Our criterion for rejection has been sufficiently rigorous that multiple scattering effects in the remaining data are believed to be insignificant. The errors in F_M include an estimate (0.15 B.M. cell^{-1}) of the least-squares error in F_N which arises from errors in the structural model used to calculate F_N. The error factor R_s, defined by $R_s = \Sigma\sigma(F_M)/\Sigma|F_M|$, is 0.045 (81 reflections) for the *a*-data set. For the *c*-data set the corresponding R_s for *l*-even reflections is 0.025 (66 reflections), while for the *l*-odd data $R_s = 0.37$ (23 reflections). The lower accuracy for *l*-odd data is a reflection of the much lower average $|F_M|$ value of 0.103 B.M. cell^{-1} for these reflections as against 3.5 for the *l*-even data. The higher absolute accuracy, $\overline{\Sigma\sigma(F_M)}$, of the *l*-odd reflections (0.04 B.M. cell^{-1}) relative to the *l*-even reflections (0.09 B.M. cell^{-1}) arises not only from the extra measuring time to improve the counting statistics of those reflections, but also from the lesser importance of systematic errors such as multiple scattering. The low-angle data which have been retained have a better relative accuracy, $\sigma(F_M)/F_M$ *ca.* 0.01, since the average values of the magnetic form factors are higher. The effect of extinction on γ may be included in the subsequent modelling of the F_M data. We quote then, in SUP 22859, magnetic structure factors $[F_M(hkl) = F_N(hkl)\gamma(hkl)]$ which still contain the effect of extinction on γ, and any beam depolarisation effect. In a case of moderate extinction, such as the present, it may be sufficient to remove (or downweight) the small number of very intense reflections (large $|F_N|$) in a crude modelling of the F_M data. We also quote values of $F_N(hkl)$ calculated from the 4.2 K nuclear structure for a hypothetical extinction-free crystal.

The sizes of the errors present in our data would therefore seem sufficiently small that we can model the spin densities expected in this complex.

QUALITATIVE DESCRIPTION OF THE DATA

In this relatively ionic complex we might expect most of the spin density to remain localised in the cobalt 3*d* orbitals. In this case we expect the *l*-odd reflections to have much smaller magnetic structure factors than the *l*-even ones, as we observe. The fact that these *l*-odd reflections do have significant structure factors

means that there *must* be some spin density non-centrosymmetric around the cobalt atom, and this we might expect if there is some covalence in the Co–Cl bond.

The difference, Δf, of the observed magnetic form factor for this complex ion from the theoretical magnetic form factor of a free Co^{2+} ion is plotted in Figure 2 for

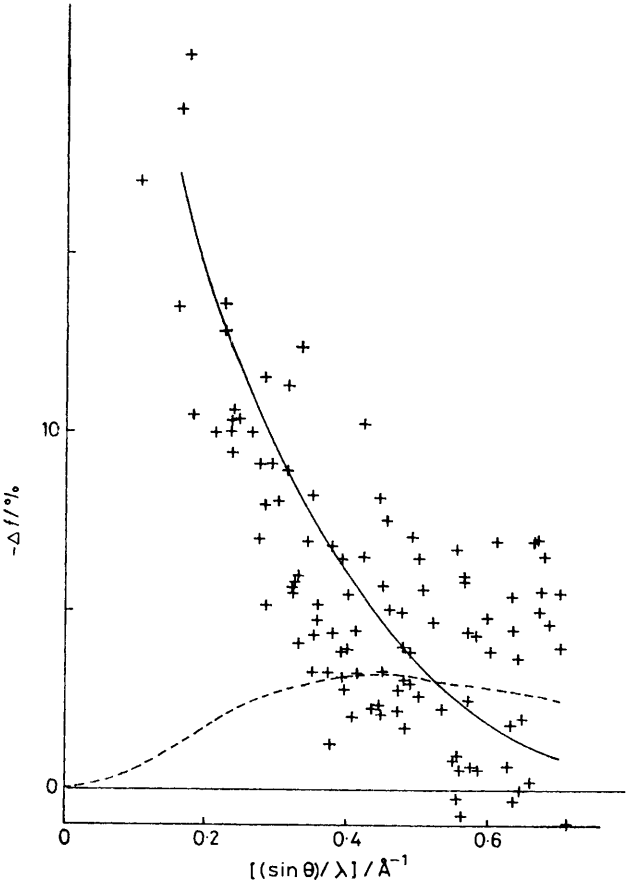

FIGURE 2 Deviation of the form factor from a free-ion form factor, Δf, plotted against $(\sin\theta)/\lambda$. The solid curve corresponds to a Δf of 0.2 (free Co^{2+} ion form factor). The dotted curve is the orbital correction to the magnetisation for the *c* data

the *l*-even reflections. The difference, while small (<20%) is significant. However most of this difference disappears if we assume that some 20% of the spin is not in the cobalt 3*d* orbitals and does not contribute strongly to the scattering at the experimental angles (*i.e.* is quite diffuse). The solid curve represents the Δf of such a '20%-delocalised' free ion. The disagreement of our data from this ion is small (<5%), but still significant compared to our experimental errors.

In Figure 3 we have plotted the observed values of Δf for the reflections *h*00 and *hh*0. The solid lines are theoretical curves plotted for an ion with an electronic configuration of $e^0t_2^{2.4}x^{0.6}$, where *e* and t_2 refer to the symmetry of the 3*d* orbitals and *x* is some unspecified very diffuse orbital. This is obviously a better approximation than a spherically symmetrical ion.

Our data thus conform well with an approximation to the $CoCl_4^{2-}$ ion in which 80% of the spin is in the 3*d* t_2 orbitals and 20% in unspecified diffuse orbitals. Any features of chemical interest, *e.g.* the *d* configuration, covalence, and the nature of the diffuse orbitals, must

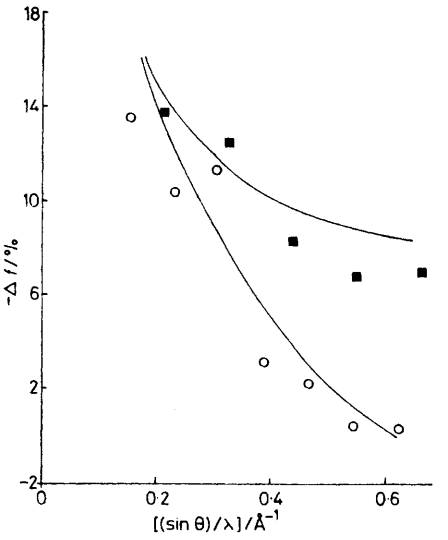

FIGURE 3 Δf, plotted for reflections *h*00 (■) and *hh*0 (○). The solid lines correspond to the theoretical curves

be derived from the small differences of the *l*-even data from this model and of the *l*-odd data from zero. We attempt such an analysis in the subsequent paper.[19]

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