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# Orbital anisotropy of the field-induced moments in chromium and vanadium

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## Abstract

The dependence of the cross-section for magnetic scattering of neutrons on the angle  $\theta_k$  between the field direction and the scattering vector has been used to study the orbital contribution to magnetic scattering from the moments aligned by a magnetic field in chromium and vanadium. The results lend support to band structure calculations which predict very high ratios of orbital to spin moments. The magnetic scattering from the moments induced in Cr and V by a 9.5 T field applied parallel to  $\langle 110 \rangle$ , in sets of crystallographically equivalent reflections having different values of  $\theta_k$ , has been determined from polarized neutron flipping ratio measurements. The results have been analysed using the tensor operator formalism. The results do not show the equatorial anisotropy predicted by a simple atomic model in which the orbital moment arises from mixing between empty  $e_g$  and filled  $t_{2g}$  states. The azimuthal variation observed suggests that the major part of the orbital moment is due to 3d states with projections of angular momentum  $m = \pm 2$ .

## 1. Introduction

The finite-temperature properties of metals in which there is more than one partly filled electron shell at the Fermi surface present an ongoing problem for both experiment and theory. One property which any model should predict is the ratio of spin to orbital contributions to the magnetization, whether it be spontaneous or induced by an applied magnetic field. Recently there has been an upsurge of interest in this ratio, triggered by the new possibility of measuring it directly using magnetic x-ray scattering [1, 2]. Such experiments have already been made on a number of magnetically ordered 3d systems, but they are as yet of limited accuracy [3, 4]. They would be very difficult to carry out on paramagnetic systems in which even a high field can only align a small moment. In the past the ratio of spin to orbital magnetization has usually been estimated from the radial dependence of the magnetic neutron scattering, using a form

factor fitting technique. In this method the experimentally determined form factor  $f(k)$  is fitted with a function of the form [5]

$$\mu_T f(k) = \langle j_0 \rangle (\mu_S + \mu_L) + \langle j_2 \rangle \mu_L + \mu_D \quad (1)$$

where  $\langle j_0 \rangle$ ,  $\langle j_2 \rangle$  are the first- and second-order radial form factor integrals for the atom [6],  $\mu_S$  and  $\mu_L$  the spin and orbital moments and  $\mu_D$  a diffuse moment.  $\mu_S$ ,  $\mu_L$  and  $\mu_D$  are the parameters of the model and  $\mu_T = \mu_S + \mu_L + \mu_D$  is the moment per atom obtained from magnetization measurements. In many of the models which are used to describe the magnetization distribution in metallic systems, the proportion of the magnetization which is ascribed to the orbital moment is a disposable parameter. However, the fact that the orbital form factor ( $\langle j_0 \rangle + \langle j_2 \rangle$ ) differs only in shape from the spin form factor ( $\langle j_0 \rangle$ ) means that, except in some special cases where the two moments are opposite and nearly equal [7], differentiation between orbital and spin moment depends very much on assumptions made about the shapes of  $\langle j_0 \rangle$  and  $\langle j_2 \rangle$  themselves. In x-ray (synchrotron) scattering the geometrical factors multiplying the orbital and spin contributions to the magnetic scattering are different [8].

The paramagnetic form factors of the 3d, 4d and 5d transition metals have been extensively studied using polarized neutron scattering [9] and many of the results have been interpreted using the above model. There is not, however, as yet general agreement between the orbital moments obtained in the polarized neutron measurements, and those predicted by theory. Particularly large proportions of orbital magnetization in the induced moments have been found in studies of chromium and vanadium [10–13]. For chromium the results suggest that 60% of the total induced moment is of orbital origin. Numerical calculations of the paramagnetic form factors of cubic transition metals, including chromium and vanadium, have been made by [14] from local density bands obtained using the KKR formalism. These calculations are in good agreement with the neutron results for chromium although they give an even higher percentage of orbital moment (82%). Unfortunately these authors do not discuss the anisotropy of the orbital scattering relative to the magnetization direction. Such anisotropy is expected because the spatial anisotropy of the electron wavefunctions depends directly on their orbital quantum numbers and hence on the orientation of any orbital moment.

## 2. Magnetic scattering by orbital moments

The crucial property exploited in this study is the way in which magnetic neutron scattering depends on the azimuthal angle  $\theta_k$  between the magnetization direction and the scattering vector  $\mathbf{k}$ . This dependence is different for the spin and orbital components of the magnetization. The magnetic scattering amplitude of a Bragg reflection with scattering vector  $\mathbf{k}$  is given by the projection on the plane perpendicular to  $\mathbf{k}$  of the  $\mathbf{k}$ th Fourier component of the magnetization distribution. If the spin–orbit coupling energy is small compared to the crystal field splitting, the orbitals occupied by unpaired electrons, and hence the distribution of spin moment, should be independent of the direction of magnetization. The amplitude of the magnetic scattering due to spin should therefore be the same (apart from the reduction factor  $\sin \theta_k$  introduced by the projection) in different equivalent directions with different values of  $\theta_k$ . The same is not true for orbital magnetization where the form of the orbital functions and hence the shape of the orbital magnetization distribution depends on the direction of the applied field.

The theory of neutron scattering by orbital moments has been treated by several authors [15–18]. Here the tensor operator method introduced in [17] and further elaborated [18, 19] has been used. These latter authors develop an expression for the magnetic interaction operator for scattering by an electron wavefunction defined by angular momentum quantum numbers  $J, M$  ( $J = L + S$ ) as a vector function  $M_{\perp}(\mathbf{k})$  of the scattering vector  $\mathbf{k}$ .

$M_{\perp}(\mathbf{k})$  is expressed in spherical components  $M_{\perp}(\mathbf{k})_q$ ,  $q = 0, \pm 1$ , where

$$\begin{aligned} M_{\perp 1} &= \sqrt{\frac{3}{8\pi}}(M_{\perp x} + iM_{\perp y}); & M_{\perp 0} &= \sqrt{\frac{3}{4\pi}}M_{\perp z}; \\ M_{\perp -1} &= \sqrt{\frac{3}{8\pi}}(M_{\perp x} - iM_{\perp y}). \end{aligned} \quad (2)$$

$M_{\perp}(\mathbf{k})$  is given in units of  $\gamma_N e^2 / mc^2$  by

$$M_{\perp}(\mathbf{k})_q = \sqrt{4\pi} \sum_{KQ} \sum_{K'Q'} Y_Q^K(\hat{\mathbf{k}}) (A(K, K') + B(K, K')) (K'Q'J'M'|JM)(KQK'Q'|1q). \quad (3)$$

The coefficients  $A(K, K')$  and  $B(K, K')$  give the orbital and spin contributions respectively and the two final brackets are Clebsch–Gordon vector-coupling (VC) coefficients. The radial dependence of the scattering is in the coefficients  $A$  and  $B$  through the form factor integrals:

$$\langle j_K(k) \rangle = \int U^2(r) j_K(kr) 4\pi r^2 dr \quad (4)$$

where  $U^2(r)$  is the radial dependence of the electron density and the  $j_K(kr)$  are spherical Bessel functions. The maximum values of the integers  $K$ ,  $K'$ ,  $Q$  and  $Q'$  depend on the wavefunction through the VC coefficient  $(K'Q'J'M'|JM)$ . The  $A(K, K') = 0$  unless  $K = K' \pm 1$ , whereas the  $B(K, K')$  are zero unless  $K = K'$  or  $K' \pm 1$ . The polarization dependence of the neutron scattering cross-section depends on just the component of  $M_{\perp}$  parallel to the polarization direction, which is in the present case parallel to the field direction. The experiment thus measures just the  $q = 0$  component of  $M_{\perp}$  and the VC coefficient  $(KQK'Q'|10)$  ensures that  $M_{\perp 0}$  is zero unless  $Q = -Q'$ .

If the wavefunctions of the electrons giving rise to the magnetization can be expressed as the sum of single-electron functions,  $\psi_i$ , expressed in an  $l, m$  basis with  $l = 2$ , then the orbital part of the magnetic interaction vector can be written as

$$M_{\perp}(\mathbf{k})_{0\text{orbital}} = \sqrt{4\pi} \sum_{K'} \left[ \sum_K A'(K, K') \sum_Q \left( Y_Q^K(\hat{\mathbf{k}}) (KQK' - Q|10) \alpha(K', Q) \right) \right] \quad (5)$$

with

$$\begin{aligned} A'(K, K') &= -(2(2K+1))^{\frac{1}{2}} (2l+1)^{\frac{3}{2}} (2K+1) (i)^{K'+1} (\langle j_{K'-1}(k) \rangle + \langle j_{K'+1}(k) \rangle) \\ &\times A(K', K', 2) \begin{pmatrix} 1 & K & K' \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} 1 & 1 & 1 \\ K' & K & K' \end{matrix} \right\}. \end{aligned} \quad (6)$$

The final two factors in equation (6), the first in brackets and the second in braces, are a  $3j$  symbol and a  $6j$  symbol respectively [21]. The form of  $A(K', K', l)$  is given in equation 6.44 of [18], which has been used to calculate  $A''(K, K') = A'(K, K') / (\langle j_{K'-1}(k) \rangle + \langle j_{K'+1}(k) \rangle)$ . The values of  $A''(K, K')$  and the VC coefficients needed to evaluate the sums in equation (5) are given in table 1. The only terms in equation (5) which depend on the actual composition of the single-electron functions  $|lm\rangle$  are the  $\alpha(K', Q)$ , given by

$$\alpha(K', Q) = \sum_{m,m'} \sum_i \langle m' | \psi_i | m \rangle (K' - Q 2m' | 2m). \quad (7)$$

If the unperturbed d functions are degenerate, orbital magnetization is due to a small imbalance, induced by the field, in the energies of orbitals with opposite values of the projection  $m$ . The perturbed functions of lowest energy have the form  $\psi_{\pm m} = \sqrt{\frac{1}{2}} ((1 + \xi_m) |m\rangle \pm (1 - \xi_m) | -m \rangle)$ , with mean orbital angular momentum  $\langle L_z \rangle = \xi_1 + 2\xi_2$ . The only non-zero values of  $\alpha$  are

**Table 1.** Coefficients needed in the calculation of  $M_{\perp 0 orbital}$ .  $A''(K, K') = A'(K, K')/(\langle j_{K'-1}(k) \rangle + \langle j_{K'+1}(k) \rangle)$ .

| $K'$            | 1             |               | 3             |               |                |               |
|-----------------|---------------|---------------|---------------|---------------|----------------|---------------|
| $K$             | 0             | 2             | 2             | 4             |                |               |
| $A''(K, K')$    | $-\sqrt{2/3}$ | $-\sqrt{1/3}$ | $-\sqrt{8/7}$ | $-\sqrt{3/7}$ |                |               |
| $Q$             | 0             | 0             | 0             | $\pm 2$       | 0              | $\pm 2$       |
| $(KQK' - Q 10)$ | 1             | $-\sqrt{2/5}$ | $3/\sqrt{35}$ | $1/\sqrt{7}$  | $-2/\sqrt{21}$ | $-1/\sqrt{7}$ |

$\alpha(1, 0) = -\sqrt{\frac{1}{6}}(2\xi_2 + \xi_1)$  and  $\alpha(3, 0) = -\sqrt{\frac{1}{14}}(\xi_2 - 2\xi_1)$ . Carrying out the summation and arranging the equation so that terms with the same radial dependence are grouped together gives

$$M_{\perp}(\mathbf{k})_{0 orbital} = \sqrt{4\pi} \left\{ \frac{1}{3}(2\xi_2 + \xi_1) \left( Y_0^0(\hat{\mathbf{k}}) - \frac{1}{\sqrt{5}} Y_0^2(\hat{\mathbf{k}}) \right) (\langle j_0(k) \rangle + \langle j_2(k) \rangle) \right. \\ \left. + \frac{2}{49}(\xi_2 - 2\xi_1) \left( \frac{3}{\sqrt{5}} Y_0^2(\hat{\mathbf{k}}) - Y_0^4(\hat{\mathbf{k}}) \right) (\langle j_2(k) \rangle + \langle j_4(k) \rangle) \right\}. \quad (8)$$

Writing the spherical harmonic functions  $Y_Q^K(\hat{\mathbf{k}})$  in terms of the spherical polar angles  $\theta_k$  and  $\phi_k$ , one gets

$$M_{\perp}(\mathbf{k})_{0 orbital} = \sin^2 \theta_k \left( \frac{1}{2}(2\xi_2 + \xi_1) (\langle j_0(k) \rangle + \langle j_2(k) \rangle) \right. \\ \left. + \frac{3}{28}(\xi_2 - 2\xi_1)(5 \cos^2 \theta_k - 1) (\langle j_2(k) \rangle + \langle j_4(k) \rangle) \right). \quad (9)$$

The spin scattering arises from the small imbalance ( $\delta$ ), induced by the field, in the occupancies of states  $\psi_i$  at the Fermi surface with spins parallel and antiparallel to the field. Since  $\delta$ ,  $\xi_1$  and  $\xi_2$  are  $\ll 1$ , terms in the sums over matrix elements, of second order and higher in  $\delta$  and  $\xi_i$  can be neglected. With this proviso, the spin scattering  $M_{\perp}(\mathbf{k})_{0 spin} / \sin^2 \theta_k$  is independent of the direction of magnetization and, unlike the orbital term, should be the same for equivalent reflections measured with different values of  $\theta_k$ . The component of the magnetic interaction vector parallel to the field can then be written as

$$M_{\perp}(\mathbf{k})_{0 spin} = \sin^2 \theta_k \sqrt{4\pi} \sum_K B'(K) \sum_Q (Y_Q^K(\hat{\mathbf{k}}) \beta(K, Q)) \quad (10)$$

with

$$B'(K) = (2K + 1)^{\frac{1}{2}} (20K0|20) \langle j_K(k) \rangle. \quad (11)$$

The part which depends on the electron wavefunction is in the terms  $\beta(K, Q)$  given by

$$\beta(K, Q) = \sum_{m, m'} \sum_i \langle m' | S_0 \psi_i | m \rangle (KQ2m' | 2m). \quad (12)$$

If the orbital states are all equally occupied,  $\beta(K, Q) = 0$  unless  $K = Q = 0$  and  $M_{\perp}(\mathbf{k})_{0 spin} = \sin^2 \theta_k \langle j_0(k) \rangle \delta$ .

### 3. Experimental details

The single crystals of pure chromium and vanadium used in the experiments were mounted with a  $[1\bar{1}0]$  axis parallel to the field direction of the 10 T superconducting magnet on the polarized neutron diffractometer D3. The chromium crystal which had dimensions  $\approx 5 \times 5 \times 10 \text{ mm}^3$  with its long axis parallel to  $\langle 1\bar{1}0 \rangle$  was cut from a large boule. The vanadium crystal was the largest

of those used in the previous form factor measurements [13]. With this crystal orientation, reflections of the form  $hhl$  have scattering vectors at  $\theta_k = 90^\circ$  to the field axis, whereas for the cubically equivalent  $hll$  and  $lhh$  reflections  $\theta_k = \cos^{-1}((h-l)/\sqrt{2(2h^2+l^2)})$ . The latter type of reflection can be measured with the normal beam diffraction geometry of D3 by tilting the detector out of the horizontal plane by an angle  $\nu = \pm \sin^{-1}(\lambda(h-l)/\sqrt{2}a)$ . Since the azimuthal anisotropy is expected to depend on  $\cos^2 \theta_k$ , no observable effect is expected unless this factor is greater than fractional uncertainty in the measurement of the magnetic amplitudes ( $\approx 3\%$ ). With  $\lambda = 0.85 \text{ \AA}$ , the  $hhl$  values giving  $\rho > 10^\circ$  ( $\cos^2 \theta_k > 0.03$ ) which were accessible within the geometric constraints imposed by the magnet were just 110, 002 and 112. The experiment on chromium was carried out at a temperature of 274 K, and that on vanadium at 100 K; in both, the magnetizing field was 9.5 T. The susceptibility of pure chromium is  $160 \times 10^{-6} \text{ emu mol}^{-1}$  and that of the vanadium sample  $266 \times 10^{-6} \text{ emu mol}^{-1}$  at the measuring temperatures. These gave induced magnetizations in 9.5 T of  $27.3 \times 10^{-4} \mu_B \text{ Cr}^{-1}$  and  $45.4 \times 10^{-4} \mu_B \text{ V}^{-1}$ . The flipping ratios measured with such low magnetization are very close to unity and long counting times were needed to obtain reasonable statistical precision. In fact, in both experiments, only the six reflections 110, 101, 002, 020, 112, 211 and their accessible equivalents were measured, each for a total of about 24 h. The results are given in table 2. The magnetic structure factors  $F_M(hkl)$  given in the table have been calculated using

$$R(hkl) = \frac{F_N(hkl)^2 + 2P^+ F_N(hkl) F_M(hkl) \sin^2 \theta_k + F_M(hkl)^2 \sin^2 \theta_k}{F_N(hkl)^2 + 2P^- F_N(hkl) F_M(hkl) \sin^2 \theta_k + F_M(hkl)^2 \sin^2 \theta_k} \quad (13)$$

in which  $R(hkl)$  is the flipping ratio,  $P^+$  and  $P^-$  are the polarizations for the two neutron spin states and  $F_N(hkl)$  is the nuclear structure factor of the reflection. For vanadium it has been shown that, because of the small coherent and large incoherent cross-sections, the contribution of neutron spin-orbit (Schwinger) scattering to the polarization-dependent cross-section cannot be neglected [20]. Due to Schwinger scattering the magnetic structure factor obtained from equation (13) exceeds the true value by an amount

$$F_s(hkl) = F_N(hkl) \frac{b'}{b} \nu \cos \theta_k \cot 2\theta_B \quad \text{with } \nu = \mu_N \frac{e^2}{2mc^2} (Z - f_X(hkl)). \quad (14)$$

$b$  and  $b'$  are the real and imaginary parts of the vanadium scattering length,  $\mu_N$  is the neutron magnetic moment in nuclear magnetons,  $Z$  and  $f_X(hkl)$  are the atomic number and x-ray scattering factor of V respectively. The corrections due to Schwinger scattering have been calculated and have already been subtracted from the magnetic structure factors listed in table 2. The corrections were found to be of the same order of magnitude as the standard deviations. Equation (13) ignores the effects of extinction which, although negligible in vanadium owing to its small coherent scattering length, are probably significant in the large single crystal of chromium. It has however been shown that when the ratio  $\gamma = F_M(hkl)/F_N(hkl) \ll 1$ , the correction for extinction takes the form [22]

$$\gamma_{corr} = \gamma_{obs} \left( 2 + \frac{F_N}{y} \frac{dy}{dF_N} \right)^{-1} \quad (15)$$

where  $y$  is the extinction factor which relates the kinematic integrated intensity of a reflection  $I(hkl)_{kin}$  to the observed integrated intensity  $I(hkl)_{obs}$ :

$$I(hkl)_{obs} = y I(hkl)_{kin} \propto y F_N^2(hkl). \quad (16)$$

For small  $\gamma$ ,  $y$  depends on  $F_N(hkl)$ , and on the physical conditions of the experiment such as wavelength and path length, which are nearly the same for equivalent reflections measured at different  $\theta_k$ . Hence by calculating an asymmetry factor

$$S(hhl) = (F_M(hhl) - F_M(lhh))/(F_M(hhl) + F_M(lhh)), \quad (17)$$

**Table 2.** Magnetic structure factors  $F_M$  and the corresponding asymmetry factors for  $hhl$  and  $lhh$  reflections of Cr and V measured in 9.5 T. The relevant form factor integrals are also listed. (Note: The magnetic structure factors,  $F_M$ , are in units of  $10^{-5} \mu_B/\text{cell}$ . The asymmetry factor  $S(hhl) = (F_M(hhl) - F_M(lhh))/(F_M(hhl) + F_M(lhh))$ .)

| $hkl$ | Chromium |            |                       |                       |                       | Vanadium |            |                       |                       |                       |
|-------|----------|------------|-----------------------|-----------------------|-----------------------|----------|------------|-----------------------|-----------------------|-----------------------|
|       | $F_M$    | $S(hhl)$   | Form factors          |                       |                       | $F_M$    | $S(hhl)$   | Form factors          |                       |                       |
|       |          |            | $\langle j_0 \rangle$ | $\langle j_2 \rangle$ | $\langle j_4 \rangle$ |          |            | $\langle j_0 \rangle$ | $\langle j_2 \rangle$ | $\langle j_4 \rangle$ |
| 110   | 312(9)   | -0.046(20) | 0.457                 | 0.166                 | 0.031                 | 361(6)   | -0.019(19) | 0.451                 | 0.169                 | 0.031                 |
| 101   | 342(10)  |            |                       |                       |                       | 375(12)  |            |                       |                       |                       |
| 002   | 215(12)  | -0.110(54) | 0.249                 | 0.187                 | 0.058                 | 223(9)   | -0.047(29) | 0.240                 | 0.190                 | 0.059                 |
| 200   | 268(23)  |            |                       |                       |                       | 225(10)  |            |                       |                       |                       |
| 112   | 178(16)  | 0.008(71)  | 0.146                 | 0.178                 | 0.074                 | 178(8)   | -0.007(27) | 0.136                 | 0.180                 | 0.076                 |
| 211   | 175(19)  |            |                       |                       |                       | 180(6)   |            |                       |                       |                       |

**Table 3.** The values of  $\theta_k G$  and  $y$  calculated for the reflections measured in the experiment. (Note:  $x = \delta/(2\xi_2 + \xi_1)$  and  $y = (\xi_2 - 2\xi_1)/(2\xi_2 + \xi_1)$ ;  $G$  is defined by equation (19).)

| $lhh$ | $\theta_k$ (deg) | $\cos^2 \theta_k$ | Chromium      |          | Vanadium      |          |
|-------|------------------|-------------------|---------------|----------|---------------|----------|
|       |                  |                   | $G(x = 0.22)$ | $y$      | $G(x = 1.11)$ | $y$      |
| 101   | 60               | 0.250             | 0.1490        | 0.81(35) | 0.0931        | 1.2(1.2) |
| 200   | 45               | 0.500             | 0.2773        | 1.26(62) | 0.1841        | 2.0(1.2) |
| 211   | 73               | 0.083             | 0.3967        | -4(42)   | 0.2783        | 4(14)    |

the effects of extinction may be largely eliminated. The asymmetry factors calculated for the three reflections 110, 002 and 112 are also listed in table 2.

#### 4. Analysis of the results

The results in table 2 show that the asymmetry factors measured for chromium and vanadium follow the same trend as one another, being small and negative for 110; larger, but still negative, for 002; and not significantly different from zero for 112. Their magnitudes are roughly proportional to  $\cos^2 \theta_k$  (table 3). The negative values suggest that  $\xi_2 > 2\xi_1$ . The values measured for chromium are approximately twice those measured for vanadium and since, as may be seen from table 2, the form factors of Cr and V are not significantly different, this implies that the proportion of orbital moment in chromium is about twice that in vanadium. This result agrees well with the band structure calculations [14] which give 85 and 46% respectively.

Recalling that  $F_M \propto M_{\perp 0}/\sin^2 \theta_k$ , and using the equations derived in section 2, the asymmetry factor may be expressed in terms of the parameters  $\xi_2$ ,  $\xi_1$  and  $\delta$ :

$$S(k, \theta_k) = -\frac{15(\langle j_2(k) \rangle + \langle j_4(k) \rangle)(\xi_2 - 2\xi_1) \cos^2 \theta_k}{28(\langle j_0(k) \rangle \delta + (\langle j_0(k) \rangle + \langle j_2(k) \rangle)(2\xi_2 + \xi_1))}. \quad (18)$$

The spin moment is proportional to  $\delta$  and the orbital moment to  $2\xi_2 + \xi_1$ . Defining  $x = \delta/(2\xi_2 + \xi_1)$  as the ratio of spin to orbital moment, and  $y$  as the ratio  $(\xi_2 - 2\xi_1)/(2\xi_2 + \xi_1)$ , the asymmetry factor becomes

$$S(k, \theta_k) = G(k, x)y \cos^2 \theta_k = -\frac{15(\langle j_2(k) \rangle + \langle j_4(k) \rangle)y \cos^2 \theta_k}{28(\langle j_0(k) \rangle(1+x) + \langle j_2(k) \rangle)}. \quad (19)$$

The values of  $\theta_k$ , for the measured reflections, and the corresponding factors  $G(k, x)$  calculated with  $x = 0.22$  and  $1.11$  for chromium and vanadium respectively [14], are listed in table 3. They have been used to determine the values of  $y$  needed to obtain the experimental result. The values obtained for  $y$  are consistent with one another within experimental error, giving mean values  $y = 0.65(24)$  ( $\xi_1/\xi_2 = -0.11(17)$ ) for chromium and  $y = 0.46(1)$  ( $\xi_1/\xi_2 = 0.03(11)$ ) for vanadium. Since a negative value for  $\xi_1/\xi_2$  is unphysical, these results suggest that in both chromium and vanadium, effectively the whole of the orbital moment is due to orbitals with  $|m| = 2$ .

## 5. Discussion

The foregoing analysis shows that the azimuthal anisotropy in the magnetic scattering from field-induced moments in chromium and vanadium is consistent with a model in which the orbital moment arises from unequal mixing between 3d states  $|\pm m\rangle$ . The numerical results suggest a much greater participation of states with  $|m| = 2$  than those with  $|m| = 1$ . This model is however not that which is generally used to account for the paramagnetic susceptibility of chromium and vanadium. It is usually assumed that in chromium the Fermi level lies between two narrow bands, the lower made up of 3d functions with mainly  $t_{2g}$  symmetry and the upper of functions with mainly  $e_g$  symmetry. Applying a magnetic field lowers the energy of the bands containing electrons with spins parallel to the field (positive spin) relative to the negative spin bands. This leads to an imbalance in the populations of positive and negative spin bands, and hence to a spin moment proportional to the magnetic field, the spin enhancement factor and the density of states at the Fermi surface. The orbital moment in this model arises from mixing of empty  $e_g$  states with occupied  $t_{2g}$  states by the potential due to the applied field. Taking the field direction  $[1\bar{1}0]$  as the  $z$ -axis and putting  $x \parallel [001]$ , the  $t_{2g}$  functions and  $e_g$  functions can be written as

$$\begin{aligned} t_0 &= \sqrt{\frac{1}{8}}(|-2\rangle + |2\rangle - \sqrt{6}|0\rangle) & e_0 &= \sqrt{\frac{1}{8}}(\sqrt{3}|-2\rangle + \sqrt{3}|2\rangle + \sqrt{2}|0\rangle) \\ t_1 &= \sqrt{\frac{1}{2}}(|-1\rangle + |1\rangle) & e_1 &= \sqrt{\frac{1}{2}}(|-1\rangle - |1\rangle) \\ t_2 &= \sqrt{\frac{1}{2}}(|-2\rangle - |2\rangle) \end{aligned} \quad (20)$$

and the three lowest-energy states of the perturbed wavefunction are

$$\begin{aligned} t_0 &= \sqrt{\frac{1}{8}}[|-2\rangle + |2\rangle - \sqrt{6}|0\rangle] \\ t_1 &= \sqrt{\frac{1}{2}}[(1 - \zeta)|-1\rangle + (1 + \zeta)|1\rangle] \\ t_2 &= \sqrt{\frac{1}{8}}[(2 - 3\zeta)|-2\rangle - (2 + 3\zeta)|2\rangle - \sqrt{6}\zeta|0\rangle] \end{aligned} \quad (21)$$

where  $\zeta = He\hbar/2m\Delta$ ,  $H$  being the applied field and  $\Delta$  the energy difference between the  $e_g$  and  $t_{2g}$  bands. The state  $t_0$  has no orbital moment,  $t_1$  has a moment  $2\zeta$  and  $t_2$  a moment  $6\zeta$ . These states are rather similar to those used in section 2 with  $\xi_1 = 2\zeta$ ,  $\xi_2 = 3\zeta$ ,  $y = -\frac{1}{8}$ ; except that the participation of the state  $|0\rangle$  in  $t_2$  leads to non-zero matrix elements  $\langle 2|t_2|0\rangle$ ,  $\langle 0|t_2|-2\rangle$  and hence to non-zero terms  $\alpha(3, \pm 2) = -\sqrt{\frac{15}{28}}\zeta$ . The corresponding extra term in  $M_{\perp}(\mathbf{k})_{0,orbital}$  is  $-\sin^2\theta_k[\frac{15}{28}\zeta(3\cos^2\theta_k - 1)\cos 2\phi_k](\langle j_2(k) \rangle + \langle j_4(k) \rangle)$ . In this expression,  $\phi_k$  is the angle in the horizontal plane between  $[001]$  and the scattering vector, and this term gives rise to anisotropy within the equatorial plane. The relative importance of the azimuthal and equatorial terms in the anisotropy with these wavefunctions is shown in table 4. It can be seen that the equatorial term ( $D$ ) makes a large contribution to the asymmetry factor which does



**Table 4.** Geometric factors and asymmetry factors for the wavefunctions of equation (21). (Note:  $\phi_k$  is measured in the (110) plane from [100].  $C(\theta_k) = \frac{3}{28}(5 \cos^2 \theta_k - 1)$  and  $D(\theta_k, \phi_k) = \frac{15}{28}(3 \cos^2 \theta_k - 1) \cos 2\phi_k$ .  $F = C(\theta_{hhl}) + D(\theta_{hhl}, \phi_{hhl}) - C(\theta_{lhh}) - D(\theta_{lhh}, \phi_{lhh}) (\langle j_2(k) \rangle + \langle j_4(k) \rangle)$ .  $S$  is the asymmetry factor calculated for vanadium when  $x$  is the ratio of spin to orbital moment. The values for chromium are virtually identical.)

| $hkl$ | $\theta_k$ (deg) | $\phi_k$ (deg) | $C(\theta_k)$ | $D(\theta_k, \phi_k)$ | $F$     | $S(x = 0.22)$ | $S(x = 1.11)$ |
|-------|------------------|----------------|---------------|-----------------------|---------|---------------|---------------|
| 110   | 90               | 90             | -0.1071       | 0.5357                |         |               |               |
|       |                  |                |               |                       | 0.0891  | -0.015        | -0.010        |
| 101   | 60               | 54.7           | 0.0268        | -0.0446               |         |               |               |
| 002   | 90               | 0              | -0.1071       | -0.5357               |         |               |               |
|       |                  |                |               |                       | -0.1336 | 0.035         | 0.024         |
| 200   | 45               | 90             | 0.1607        | -0.2679               |         |               |               |
| 112   | 90               | 35.3           | -0.1071       | -0.1786               |         |               |               |
|       |                  |                |               |                       | -0.1226 | 0.044         | 0.033         |
| 211   | 73               | 64.8           | -0.0625       | 0.2556                |         |               |               |

not follow the trend of the observations. The experimental results suggest that the states at the Fermi surface whose mixing gives rise to the orbital moments are filled  $t_{2g}$  states  $\sqrt{\frac{1}{2}}(|-2\rangle - |2\rangle)$  and empty states having the form  $\sqrt{\frac{1}{2}}(|-2\rangle + |2\rangle)$  rather than the form  $e_0$  of equation (20).

It is perhaps not surprising that the band model wavefunction is not able to account for the experimental data, since it assumes infinitely narrow 3d bands and takes no account of the band structure. A better model calculation could be made if the method developed by [14] were extended to give the asymmetry factors. It would be interesting to know whether a realistic band structure model will reproduce the results measured here.

## 6. Conclusions

Polarized neutron flipping ratios in chromium and vanadium have been measured for sets of crystallographically equivalent reflections which had their scattering vectors differently inclined to a 9.5 T field applied parallel to  $[1\bar{1}0]$ . Magnetic structure factors derived from these results show a significant azimuthal anisotropy. Such anisotropy is predicted in the orbital scattering from a simple model in which the orbital moment arises from the inequality induced by the field between the mixing parameters of 3d states  $|\pm m\rangle$ . The magnitude of the anisotropy is consistent with the predicted orbital moments only if the participation of electrons in states with  $m = \pm 2$  strongly outweighs that of those with  $m = \pm 1$ . On the other hand, in a model in which the orbital moment arises from mixing between empty  $e_g$  states and filled  $t_{2g}$  ones, the azimuthal anisotropy is outweighed by anisotropy in the (110) plane perpendicular to the field, and this anisotropy is not present in the data. The results suggest that the band orbitals are such that the active empty states at the Fermi surface have the form  $\sqrt{\frac{1}{2}}(|-2\rangle + |2\rangle)$  and contain a negligible contribution from  $|0\rangle$ .

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