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Non-spherical magnetic moment in MnAlGe

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Abstract. The magnetic structure factors of MnAlGe (space group $P4/nmm$) measured with polarised neutrons have been expressed in terms of the magnetic moment of the Mn atom (site symmetry tetrahedral with tetragonal distortion), the Bessel transforms $\langle j_n \rangle$ of the Mn radial functions and the fractional occupancies of the moment density in the various crystal field orbitals. The measured structure factors were least-squares fitted with the theoretical expression involving $\langle j_n \rangle$ appropriate to the Mn^0, Mn^+ and Mn^{2+} atoms. The best fit was got using Mn^0 transforms, yielding $1{\cdot}45\,\mu_B$ as the Mn magnetic moment. The fractional occupancies of the moment density in the crystal field orbitals A_{1g}, B_{1g} E_g and B_{2g} were obtained. This analysis shows the magnetic moment to be highly non-spherical with a large fractional occupancy (38%) in the A_{1g} orbital directed along the tetragonal axis while the fractional occupancies of B_{1g} and B_{2g} are found to be 31% and 30% respectively. The fractional occupancy of the moment in the E_g orbital directed towards the Ge and Al atoms is very low (1%). The spatially averaged moment density of Mn in MnAlGe is more diffuse than that of Mn I and Mn II in isostructural Mn_2Sb.

Keywords. Magnetic moment density; polarised neutron diffraction; Mn form factor; MnAlGe.

1. Introduction

The intermetallic ternary compound MnAlGe crystallises in a tetragonal structure (space group $P4/nmm$) where the Mn atoms occupy the special positions $2a$ at (000) and $(\frac{1}{2}\,\frac{1}{2}\,0)$, while the Al and Ge atoms are at the general positions $2c$ $(0\,\frac{1}{2}\,z)$ and $(\frac{1}{2}\,0\,\bar{z})$, and $(0\,\frac{1}{2}\,\bar{z}')$ and $(\frac{1}{2}\,0\,\bar{z}')$. The neutron diffraction investigations in a polycrystalline specimen of MnAlGe (Satya Murthy *et al* 1969) showed $z = 0{\cdot}273$ and $z' = 0{\cdot}720$ and the magnetic moment on the Mn atom to be $1{\cdot}40\mu_B$. The fairly large anisotropy along the tetragonal axis observed in this compound (Wernick *et al* 1961), the rather low magnetic moment carried by the manganese atom and the similarity of its structure with ferrimagnetic Mn_2Sb makes it an interesting substance for the investigation of the magnetic moment distribution by polarised neutrons.

We have determined accurately the structural parameters in single crystal specimens of MnAlGe using unpolarised neutrons. Next, using polarised neutrons, the magnetic structure factors have been determined in the [001] zone. These

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magnetic structure factors have been interpreted in the framework of an appropriate theoretical model to obtain the 3d-like moment of the manganese atom as also the fractional orbital populations of the unpaired electron density in the various crystal field sub-levels.

2. Experimental

2.1. *Unpolarised neutron data*

Single crystal specimens (cut from the same piece) were aligned for the [110] and [010] zones. Most of the reflections required for the structure analysis are contained in these two zones. Some of the reflections in the [001] zone have sizeable magnetic contributions; however it would require magnetic fields of the order of 36 kOe (Wernick *et al* 1961) to separate them out from the total Bragg intensities. Hence the unpolarised neutron data were confined to the first two zones. Using unpolarised neutrons of wavelength 1·24 Å, 86 reflections (including 58 equivalent ones) in the [110] zone and 59 reflections (including 22 equivalent ones) in the [010] zone were scanned upto $\sin\theta/\lambda = 0{\cdot}7$ Å^{-1}. From the observed intensities, it was found that the crystal suffered from secondary extinction. The observed structure factors of all these reflections were refined by a full matrix least-squares analysis which included an evaluation of secondary extinction. In this analysis the small magnetic contributions to the reflections (largest being $\sim 5\%$) were neglected and the structural parameters were obtained. Subsequently, the magnetic parameters determined from the polarised neutron work were put in and the final structural parameters obtained were:

Temperature factor $B = 0{\cdot}85 \pm 0{\cdot}04 \times 10^{-16}$ cm^2

$z = 0{\cdot}299 \pm 0{\cdot}002$

$z' = 0{\cdot}724 \pm 0{\cdot}001$

Extinction constant $g = 170 \pm 30$.

Occupancy factors $a_{Mn} = 1{\cdot}00$, $a_{Al} = 0{\cdot}98$ and $a_{Ge} = 0{\cdot}90$. The agreement factor of the analysis was 7·2%. The Mn atoms were found to order exclusively on the 2*a* sites.

2.2. *Polarised neutron data*

For the polarised neutron diffraction study, a single crystal specimen aligned for the [001] zone was used. Peak intensities were measured for the two spin states of the incident polarised neutrons to obtain the polarisation ratio R_{obs} defined as:

$$R_{obs} = \frac{I^+_{obs}}{I^-_{obs}} = \frac{1 + \gamma^2 + 2PD\gamma}{1 + \gamma^2 - 2PD\gamma\ (2F - 1)} \qquad (1)$$

where $\gamma = M/N$ whhre M and N are the magnetic and nuclear structure factors respectively, P the incident neutron polarisation, $1 - D$ the depolarisation of the beam in the crystal and F the flipping efficiency of the neutron resonant flipper (P was 0·95 and F was 0·97).

The polarisation ratios of equivalent reflections with different path lengths were found to be different, owing to the presence of secondary extinction. The most significant difference in the polarisation ratio was seen in the (110) reflection (*see*

Table 1. Polarised neutron measurements on MnAlGe in [001] zone. $\bar{t}$ is the effective path length in the crystal; R_{obs} and R_{corr} denote tne observed and extinction corrected (with $g = 250$) polarisation ratios respectively.

hkl	$\bar{t}$ (cm)	R_{obs}	R_{corr}	Magnetic structure factors in μ_B/unit cell
(110)	0·100	0·621±0·010	0·594	1·525±0·016
(1$\bar{1}$0)	0·400	0·676±0·010	0·592	1·538±0·016
(200)	0·160	2·250±0·018	2·294	1·236±0·027
(220)	0·110	1·498±0·013	1·506	0·608±0·019
(2$\bar{2}$0)	0·275	1·451±0·019	1·471	0·573±0·028
(310)	0·125	0·866±0·010	0·861	0·442±0·025
(3$\bar{1}$0)	0·275	0·870±0·010	0·860	0·448±0·028
(400)	0·245	1·114±0·011	1·121	0·169±0·016
(330)	0·120	0·941±0·013	0·939	0·187±0·036
(420)	0·145	1·061±0·027	1·062	0·089±0·040
(510)	0·150	0·970±0·014	0·966	0·104±0·040
(440)	0·150	1·091±0·041	1·092	0·131±0·061
(530)	0·150	0·962±0·017	0·961	0·117±0·048
(600)	0·250	1·067±0·085	1·067	0·096±0·126

table 1) where the path lengths for the two equivalent reflections differ by a factor of 4 (1 mm and 4 mm). Applying Zachariasen's correction for extinction, the observed polarisation ratio R_{obs} gets modified as:

$$R_{obs} = \frac{I^{+}_{obs}}{I^{-}_{obs}} = R_{corr} \frac{(1 + 2gQ^{-}\bar{t})^{\frac{1}{2}}}{(1 + 2gQ^{+}\bar{t})^{\frac{1}{2}}} \tag{2}$$

where R_{corr} is the polarisation ratio in the absence of extinction, $\bar{t}$ is the effective path length in the crystal, g is the extinction parameter and $Q^{\pm}$, the crystal reflectivities for the two spin states of the incident neutrons. Since Q^{+} and Q^{-} are respectively proportional to $(N + M)^2$ and $(N - M)^2$, from eq. (2) it is clear that R_{corr} can be sought only by an iterative procedure. As an example, we consider the pair of reflections (110) and (1$\bar{1}$0) where the extinction effect was most significant. Taking the calculated values of N (from the structural parameters obtained with the unpolarised neutron data) and obtaining M from eq. (1) (neglecting extinction and depolarisation), different values of g were tried using eq. (2) till good convergence was obtained for R_{corr} with $g = 250$. Similar convergence with $g = 250$ was obtained for the other two pairs of reflections, namely, (220) and (310), where the path lengths for equivalent observations differed. Using this value of g, the observed polarisation ratios for all the reflections taken in this zone were

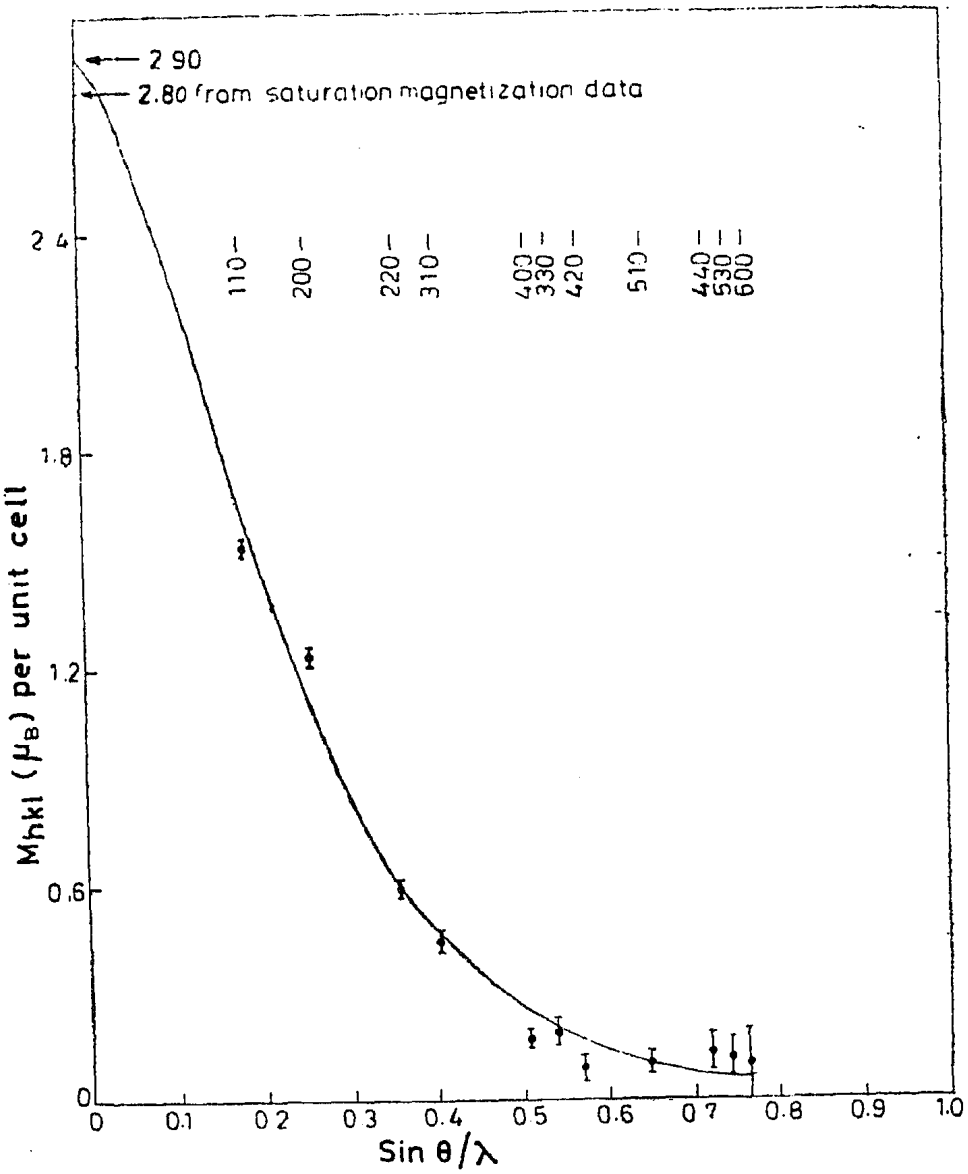

Figure 1. Observed magnetic structure factors (•) and calculated magnetic structure factors (continuous line) with $\mu = 1{\cdot}45\mu_B$, $\epsilon = -0{\cdot}242$, $\delta = 0{\cdot}469$ and $(B_{1g} - B_{2g}) = 0{\cdot}01$.

corrected for extinction and are shown in table 1. Good agreement between polarisation ratios measured on equivalent reflections gave confidence that effects due to depolarisation and Renninger scattering were small and in any case negligible when compared to extinction effects.

From the measured polarisation ratios corrected for extinction, the magnetic structure factors M were obtained using eq. (1) and are shown in table 1. These magnetic structure factors are also plotted in figure 1. (The magnetic form factors are not plotted for reasons discussed below.)

3. Results and discussion

The interpretation of the measured magnetic form factors in the 3d metals (Shull and Yamada 1962, Moon 1964, Mook 1966) have been carried out with some success in terms of a 'free atom' moment density modified by appropriate crystalline field effects. Indeed, Stern (1959) has shown theoretically that the wave functions of the magnetic electrons near the top of the d-band are very similar to the atomic wave functions. The pseudo-potential calculations in nickel (Hodges *et al* 1966) and the APW calculations in cobalt (Hodges and Ehrenreich 1968)

have also demonstrated the atomic character of the magnetic electrons. Hence the concept of a 'local' moment and the interpretation of measured magnetic form factors in terms of free-atom calculations have some theoretical justification. We, therefore, proceed now to analyse our results in terms of free-atom-like pure d orbitals modified by the crystalline field, although the ultimate validity of such a procedure is to be justified on rigorous theoretical grounds.

The site symmetry of the Mn atom is tetrahedral with a tetragonal field provided by the surrounding Ge and Al atoms. This tetragonal field splits the d orbitals into the following symmetry orbitals:

$$A_{1g}\,(d_{z^2}),\ B_{1g}\,(d_{x^2-y^2}),\ E_g\,(d_{zx},d_{zy}) \quad \text{and} \quad B_{2g}\,(d_{xy}).$$

The magnetic structure factor M_{hkl} of any reflection, therefore, can be expressed in terms of the principal scattering factors given by Weiss and Freeman (1959) and can be cast in the following form :

$$M_{hkl} = 2\mu \langle j_0 \rangle + 2\mu\epsilon E_{hkl} \langle j_2 \rangle + 2\mu\delta D_{hkl} \langle j_4 \rangle + 2\mu\,(B_{1g} - B_{2g})\, B_{hkl} \langle j_4 \rangle \tag{3}$$

where the $\langle j_n \rangle$'s are the spherical Bessel transforms of the 3d Hartree-Fock radial functions tabulated by Watson and Freeman (1961) and μ is the magnetic moment carried by the Mn atom. The symmetry parameters ϵ and δ are

$$\epsilon = A_{1g} - B_{1g} - B_{2g} + E_g/2$$

$$\delta = A_{1g} + \tfrac{1}{6} B_{1g} + \tfrac{1}{6} B_{2g} - 2E_g/3$$

where the symbols A_{1g}, B_{1g}, B_{2g} and E_g represent the fractional orbital populations of the unpaired electron density in their respective crystal field levels. The geometrical factors are

$$E_{hkl} = \frac{5}{7}(1 - 3\cos^2\beta)$$

$$D_{hkl} = \frac{9}{28}(3 - 30\cos^2\beta + 35\cos^4\beta)$$

$$B_{hkl} = \frac{15}{8}\sin^4\beta\cos 4\alpha$$

where β is the angle between the scattering vector hkl and the tetragonal axis and

$$\cos 4\alpha = \frac{h^4 + k^4 - 6h^2k^2}{(h^2 + k^2)^2}$$

The observed magnetic structure factors were least-squares fitted to eq. (3) using the spherical Bessel transforms appropriate to the Mn^0, Mn^+ and Mn^{2+} configurations (Watson and Freeman 1961) and with μ, ϵ, δ and $(B_{1g} - B_{2g})$ as variable parameters. The best fit was obtained with the Mn^0 spherical Bessel transforms, yielding the 3d-like magnetic moment of the Mn atom to be $1{\cdot}45\mu_B$. The other parameters were refined to be as follows: $\epsilon = -0{\cdot}242$, $\delta = 0{\cdot}469$ and $B_{1g} - B_{2g} = 0{\cdot}01$. In figure 1 the solid line has been drawn through the calculated magnetic structure factors. The saturation magnetisation value (Shibata *et al* 1973) of $1{\cdot}40\mu_B$/atom is about 3·5% lower than the 3-d-like moment by the present analysis. On this basis, however, it is difficult to argue for the presence of a negative conduction electron polarisation of $0{\cdot}10\mu_B$ per unit cell. [It may be remarked that the zonal

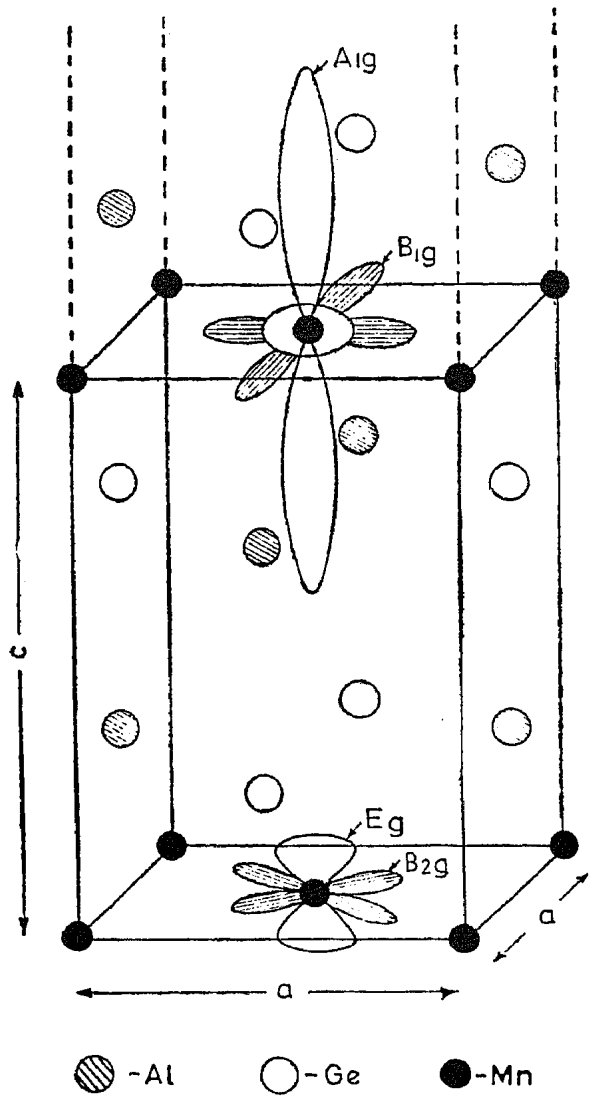

Figure 2. Pictorial representation of the four symmetry orbitals of the Mn atom in MnAlGe. For clarity, all the four orbitals have not been shown on the same Mn atom.

data were regarded as insufficient to justify a Fourier projection of the moment density on the (001) plane.] The low magnetic moment on the Mn atom points to the highly ' covalent ' character of the bonding of the Mn atoms with the surrounding Ge and Al atoms. Indeed, the subsequent analysis shows the fractional occupation of the unpaired electron density in the E_g symmetry orbital directed along the Ge and Al atoms to be very low. The rather large reduction of the moment is perhaps due to the competition between the crystal field (highly covalent in character) and the exchange field. The fact that Mn I has the same moment in MnAlGe as in isostructural Mn_2Sb (Alperin *et al* 1963) shows the situation to be more complex than what can be visualised on a purely local orbital picture. Hence a full band structure calculation on MnAlGe is warranted which does not exist and is difficult to achieve at the moment. We shall therefore pursue the analysis in terms of crystal field orbitals.

The present analysis yields the following fractional orbital populations of the various symmetry functions of the d orbitals of the Mn atom:

$$A_{1g}\,(d_{z^2}) = 0{\cdot}38$$

$$B_{1g}\,(d_{x^2-y^2}) = 0{\cdot}31$$

$$B_{2g}\,(d_{xy}) = 0{\cdot}30$$

$$E_g\,(d_{zx},\, d_{zy}) = 0{\cdot}01$$

The non-spherical distribution of the magnetic moment density is obvious. In figure 2 an attempt is made to convey a pictorial impression of the asphericity of this moment density. The $(A_{1g} + B_{1g})$ functions which correspond to the e_g function of the cubic symmetry contains 69% of the unpaired electrons. In the basal plane there is an absence of the 'ligands' and a near symmetrical disposition of the magnetic atoms which explains perhaps the almost equal fractional occupancies of the B_{1g} and B_{2g} orbitals. The most striking feature of this analysis is the large fractional occupancy of the A_{1g} (d_{z^2}) orbital disposed along the tetragonal axis which happens to be the direction of easy magnetization in the crystal (Wernick *et al* 1961). This observation is consistent with the large fractional occupancies of orbitals directed along the easy directions of magnetization in other crystals such as in Ni ($T_{2g} = 81\%$) (Mook 1966) and in Fe ($e_g = 53\%$) (Shull and Yamada 1962).

After estimating the asphericity of the magnetic moment in terms of the fractional occupancies of the various crystal field orbitals, we next compare the spatially averaged moment density distribution with those obtained in other intermetallic compounds and alloys of Mn. The smoothened curve through the experimental magnetic structure factors was Fourier transformed to obtain the spherically averaged moment density distribution $r^2\rho\,(r)$. Figure 3 shows the $r^2\rho\,(r)$ distribution of the Mn moment in MnAlGe along with the cylindrically averaged moment density distributions of Mn I and Mn II in the isostructural crystal Mn_2Sb (Alperin 1974), all the three normalized to the same peak height. Though all the three distributions peak around 0·46 Å, it is observed that the moment density distribution

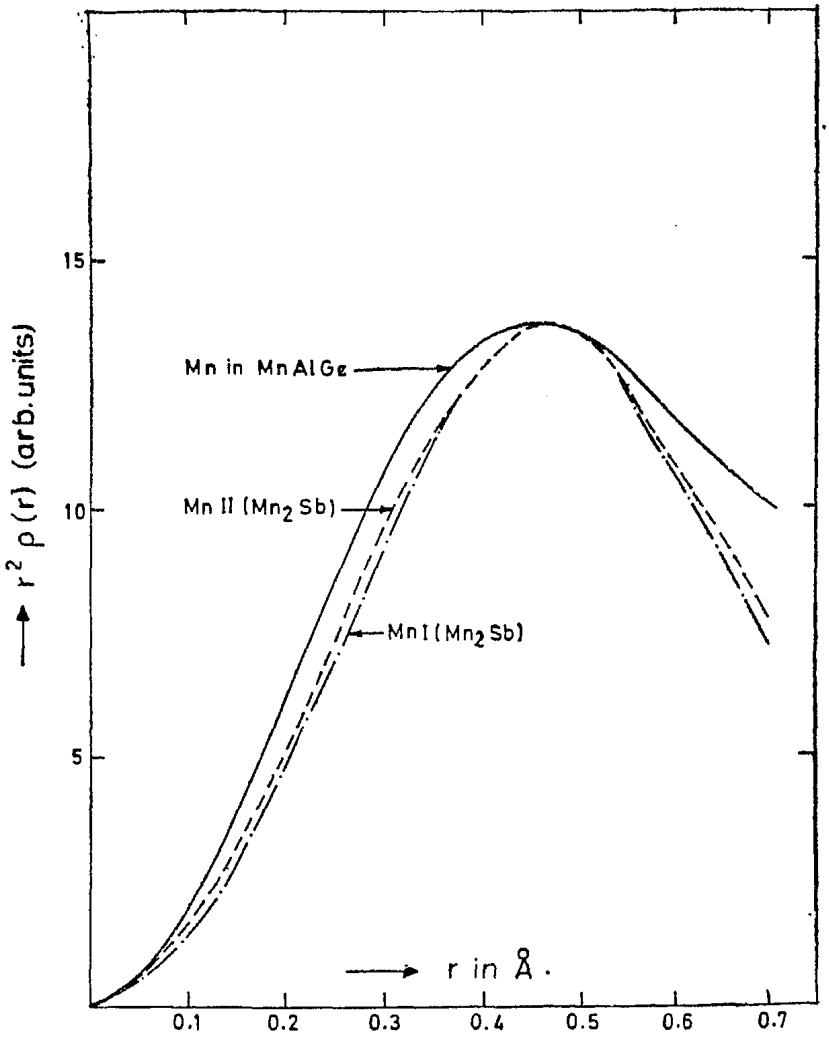

Figure 3. Radial moment density distribution of Mn in MnAlGe and of Mn I and Mn II in Mn_2Sb (*see* text).

of Mn in MnAlGe is more diffuse than either Mn I or Mn II in Mn_2Sb. Mn I (magnetic moment $1{\cdot}48\,\mu_B$) and Mn II (magnetic moment $2{\cdot}66\,\mu_B$) (Alperin *et al* 1963) have nearly the same radial distributions and both are more compact than the calculated Mn^{2+} radial distribution (Watson and Freeman 1961). The radial distribution features of manganese seen in MnAlGe and in Mn_2Sb indicate that there is no correlation between the magnetic moment and the degree of " ionicity " of the manganese atom. This is further corroborated by the most recent measurement of the manganese form factor in $MnPt_3$ (Mn moment $3{\cdot}68\,\mu_B$) (Menzinger *et al* 1972) and in $Mn_{1-x}Ir_x$ (Mn moment $\sim 2{\cdot}4\,\mu_B$) (Yamaoka *et al* 1974) where the measured Mn radial distributions lie close to the calculated Mn^{2+} distribution. However, Suzuki *et al* (1973) observed that in ferromagnetic $Mn_{1+\delta}Sb$ ($\delta = 0{\cdot}05$ and $0{\cdot}16$) having the NiAs type of structure with Mn moment of $3{\cdot}5\,\mu_B$, the moment density distribution compares well with the calculated Mn^0 one.

4. Conclusion

The principal outcome of this study is the presence of a highly non-spherical distribution of the moment density with a large fraction disposed along the anisotropy (tetragonal) axis. The 3d-like moment per atom obtained in the present study is quite low and not much different from that got from the saturation magnetization measurement. The spatially averaged moment density distribution in MnAlGe is more diffuse than that in isostructural Mn_2Sb or in other intermetallic systems like $MnPt_3$ and $Mn_{1-x}Ir_x$, but compares well with that in $Mn_{1+\delta}Sb$.

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