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A polarised neutron study of magnetic moment density in Cu_2MnAl

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Abstract. A polarised neutron study of the ferromagnetic Heusler alloy $Cu_2Mn_{0\cdot863}Al_{1\cdot057}$ has been made. It has been concluded that the magnetic moment density is primarily situated on the Mn ions. On assigning the Mn-moment value, the observed magnetic form factor is found to be in good agreement with the Mn^{2+} free ion form factor calculated by Watson and Freeman. A slight asphericity has been observed in the moment density. It is estimated that there are about 3% excess 3*d*-electrons in the Eg states compared to spherical distribution. There is evidence of a very small positive polarisation of the Cu atoms. No appreciable conduction electron polarisation is found.

Keywords. Cu_2MnAl; polarised neutron diffraction; Mn form factor; magnetic moment density.

1. Introduction

Magnetic moment density has been studied in a single crystal of ferromagnetic Heusler alloy $Cu_2Mn_{0\cdot863}Al_{1\cdot057}$, with an $L2_1$ structure (Pearson 1958), using polarised and unpolarised neutron diffraction measurements at room temperature. The crystal used in the present measurements is deficient in Mn and has a slight excess of Al in comparison to the fully ordered alloy of Cu_2MnAl. A preliminary report of these measurements had been presented earlier (Rakhecha *et al* 1976). An unpolarised neutron powder diffraction study of ordered Cu_2MnAl was first carried out by Felcher *et al* (1963), who confirmed from their work the fully ordered Heusler structure. Polarised neutron measurements have been made later by Forsyth (1963) and by Takata (1965). No detailed results are available in literature on Forsyth's measurements, whereas Takata's measurements are confined mainly to shim ratios for 16 reflections in the [110] zone. Takata inferred a moment of $3\cdot2\ \mu_B$ on individual Mn ions at 293°K (which is the saturation moment at 293°K) and concluded that there was no asphericity in the moment distribution. The present measurements are more extensive than any of those reported previously. The number of reflections studied (47) is more and of these 20 reflections (odd Miller indices) are much weaker in intensity and thus free from extinction. The overall accuracies in magnetic structure amplitudes are better than 2% for most low angle reflections (particularly of

A list of symbols appears at the end.

odd indices) and it has been possible to determine the asphericity of moment density at the Mn sites.

2. Neutron structure amplitudes in Cu_2MnAl

The crystal structure consists of four interpenetrating fcc sublattices. The coordinates of the sites designated A, B, C and D are given in figure 1. The Mn-Site (B-site) is a centre of inversion and the nuclear structure amplitudes ($N(hkl)$) referred to this site as origin are real and fall into three categories having respectively three types of structure amplitudes (Webster 1969). One of these has odd Miller indices and the other two have even Miller indices with $(h+k+l)/2$ even or odd. These are shown in table 1.

The magnetic structure amplitudes ($M(hkl)$) are obtained by replacing the nuclear scattering amplitudes (b) for the individual sites by the respective magnetic amplitudes (p).

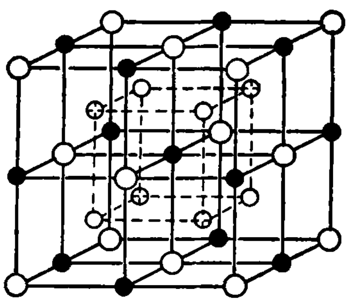

Figure 1. The Heusler $L2$ structure is shown along with the positions of sites designated A(Cu), B(Mn), C(Cu) and D(Al).

Table 1. Three types of reflections in Cu_2MnAl

hkl	Reflection type	Structure amplitude* $N(hkl)$
all odd	I	$4(b_B-b_D)$
all even		
$(h+k+l)/2$ odd	II	$4[(b_A+b_C)-(b_B+b_D)]$
$(h+k+l)/2$ even	III	$4[(b_A+b_C)+(b_B+b_D)]$

*For Cu_2MnAl, $b_A=b_C=b_{Cu}$, $b_B=b_{Mn}$, $b_D=b_{Al}$

3. Experiment and analysis

3.1. *Unpolarised neutron measurements*

The nuclear scattering parameters were determined from unpolarised neutron Bragg intensity measurements ($\lambda = 1{\cdot}24\,\text{Å}$) for 11 high-angle reflections in [110] zone. The crystal dimensions were $1 \times 1 \times 10\ \text{mm}^3$ with the long axis along [110]. The nuclear scattering lengths for Mn, Cu and Al were respectively taken as $-0{\cdot}37$, $0{\cdot}76$ and $0{\cdot}35 \times 10^{-12}$ cm and the constraint

$$2\,\langle b_{\text{Cu}}\rangle + \langle b_{\text{Mn}}\rangle + \langle b_{\text{Al}}\rangle = 1{\cdot}57\times 10^{-12} \tag{1}$$

was used from the known composition of the crystal. The average amplitudes (denoted by $\langle \ldots \rangle$) for the Cu-, Mn- and Al sites were determined from the refinement for several fixed values of extinction parameter g in Zachariasen theory. The R factor was seen not to change significantly for g values as large as 1500 ($R = 0{\cdot}053$ for $g = 0$ and $R = 0{\cdot}051$ for $g = 1500$) and thus the extinction was not established from these measurements. The extinction was ascertained to be negligible, however, from the polarised neutron data analysis as will be seen in the next section. The refined parameters are ($g = 0$)

$$\begin{aligned}
\langle b_{\text{Cu}}\rangle &= 0{\cdot}75 \times 10^{-12}\ \text{cm}\\
\langle b_{\text{Mn}}\rangle &= -0{\cdot}29 \pm 0{\cdot}01 \times 10^{-12}\ \text{cm}\\
\langle b_{\text{Al}}\rangle &= 0{\cdot}36 \pm 0{\cdot}01 \times 10^{-12}\ \text{cm}\\
B &= 1{\cdot}20 \pm 0{\cdot}02 \times 10^{-16}\ \text{cm}^2
\end{aligned} \tag{2}$$

A lumped temperature factor was employed for all the sites. The average amplitudes for the Cu- and Al- sites differ only slightly from the Cu- and Al- amplitudes, and thus show that the disorder, if any, is negligibly small. However, due to the presence of about 2% vacant sites and to the indicated errors on the deduced parameters, it is not possible to establish the precise nature of disorder.

3.2. *Polarised neutron measurements*

Three samples cut from the same parent crystal were employed in the polarised neutron measurement (wavelength $\lambda = 0{\cdot}92$ Å, polarisation efficiency $P = 0{\cdot}93$, flipping efficiency $f = 0{\cdot}99$). The crystals were nearly parallelopiped in shape, about 1 mm thick and 10 mm long. They were polished using fine emery paper but tended to blacken slightly with the passage of time. A saturating magnetic field of 8 kOe was used throughout the measurements. The long axis for the three cyrstals was respectively along [100], [110] and [112] directions. Polarisation ratios were measured for 47 independent reflections in these three zones. Ratios for most reflections were measured for at least two equivalents in the same zone. Also most reflections common to different zones were measured separately to detect any multiple Bragg effects. Some variation was observed in the ratios for some reflections from measurement to measurement, in the same zone and in different zones, owing possibly to the latter effect.

The γ ($=M/N$) values were derived for individual measurements for $g = 0$ and by taking the beam depolarisation* in the sample to be 1% per mm. The γ values of the three groups of reflections (table 1) are plotted in figures 2 (a-c) as a function of $\sin\theta/\lambda$ (θ = Bragg angle). They show a nearly smooth behaviour. The size of the bands for some reflections in these figures show the spread of their observed values. The spread is somewhat large for (220), (222) and (400) but for (200) the value is the same in both [001] and [110] zones. In the former the spread could possibly arise from multiple Bragg effects. The reflections with odd indices are the weakest in intensity and therefore the extinction is also the least important for these reflections. We expect that the behaviour of γ values for these reflections should closely represent the experimental Mn form factor apart from normalisation. In figure 2a, we have plotted alongside the experimental points, the Mn^{2+} free ion form factor of Watson and Freeman (1961), multiplied by a scaling factor of 1·23. It is seen clearly that the free ion scaled curve matches the experimental points very well. If no depolarisation is considered the [111] value is about 7% lower and that of (311) by about 1%. This sensitivity of (111) reflection to depolarisation has been used to fix the depolarisation value as pointed out in the foot note.

The γ-values for the even reflections with $(h+k+l)/2$ odd also scale quite closely to the Mn^{2+} form factor, particularly if the largest of the observed γ-values for (222) in [110] zone is considered (figure 2b). In the case of $(h+k+l)/2$=even, the experimental points do not scale to the Mn^{2+} curve so well; the two differ somewhat systematically (figure 2c). This, however, is not due to extinction because extinction-wise these reflections should have been equally affected as the other group of even reflections (because $b_{Mn}+b_{Al}$ is very small and all even reflections have almost the same nuclear structure factor). These reflections are order-independent and we may suspect that some contributions which cancel for $(h+k+l)/2$ odd, do not do so here. The behaviour of γ for the three groups of reflections suggests that the magnetic moment is localised on the crystal sites with an Mn^{2+} free ion form factor. This latter fact is most clearly demonstrated from the odd reflections, which get a magnetic contribution only from the *B*-sites. The proportionality of the γ for the weaker odd reflections and the stronger even reflections (particularly $(h+k+l)/2$ odd) shows also that the extinction correction is negligible.

3.3. *Refinement of experimental M/N values: magnetic moments and asphericity*

In view of the non-perfect composition of the crystal we analysed the γ-values directly in terms of average nuclear scattering parameters, magnetic moments at different sites and model form factors. The g value for Cu_2MnAl is very close to 2 (=2·01)

*(111) is a polarising reflection and the deduced M/N value for this reflection is very sensitive to the assumed depolarisation in the sample. (200) reflection which is very close in angle to (111) does not depend sensitively on depolarisation. This fact has been exploited in fixing the depolarisation value of 1% per mm in the sample so that the (111) γ-value falls on the scaled Mn^{2+} form factor curve just as the (200) point does (see figures 2 (a-c) and the following text). The errors on M/N values have been deduced by assuming 0·5% error on P and f. The error due to the lack of depolarisation value is estimated to be less than 1% for reflections other than (111). The extent to which the assumed value of depolarisation represents the actual value will render this error to be even smaller.

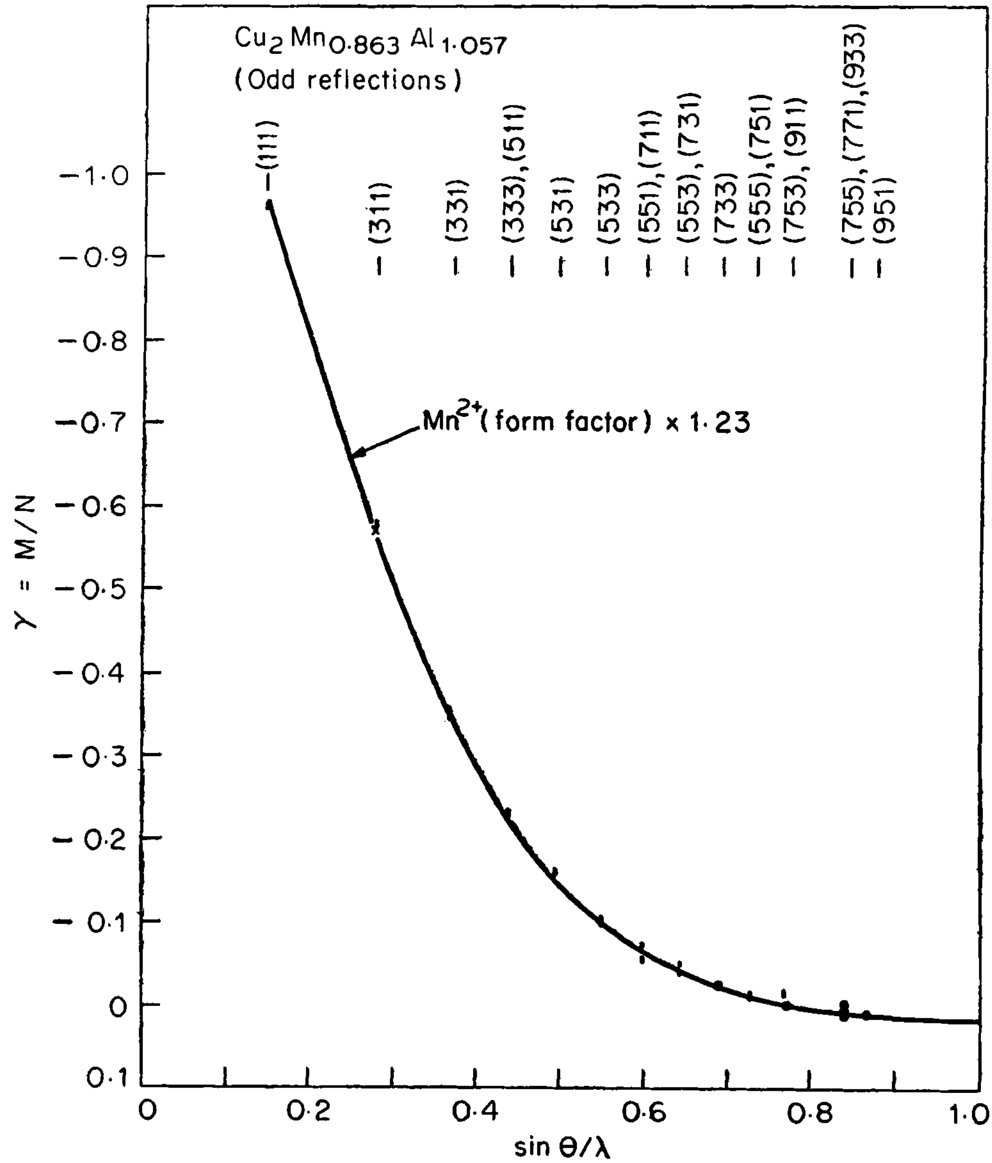

Figure 2. $\gamma = M/N$ against $\sin \theta/\lambda$ for the three types of reflections. (a) odd reflections.

and the moment density can therefore be considered to be spin-only (Scott 1962). We assumed the Mn^{2+} free ion form factor for the Mn-sites as argued before and also for the nominal Al-sites when Mn-atoms are presumed to go to these wrong sites due to disorder. For Cu-sites we used the form factor for Cu^{2+} (by Watson) as taken from Menzinger *et al*'s (1969) paper.

The asphericity of the Mn-site moment, as indicated from the γ-values in figures 2 (a-c) has been considered in a pure (octahedral) crystal field. The Mn-site form factor is assumed as (Weiss and Freeman 1959).

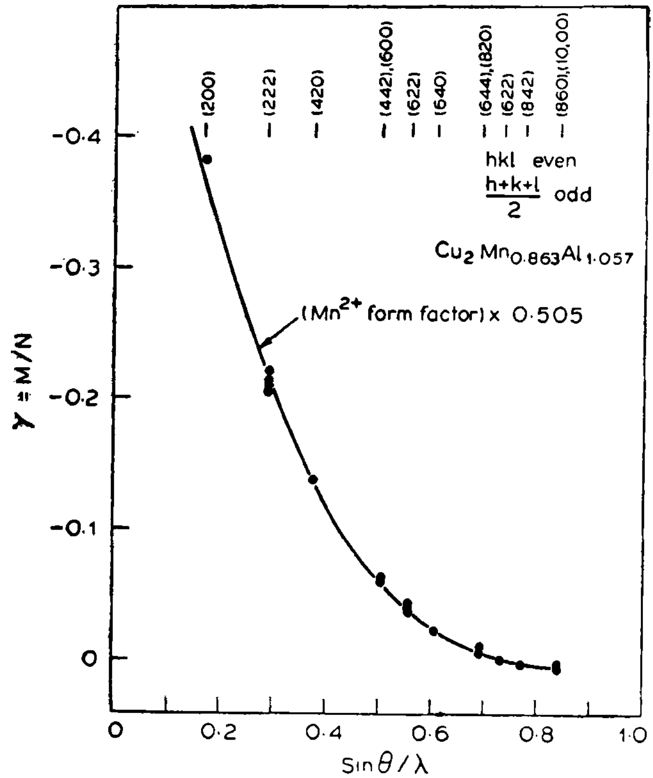

Figure 2 (b). Even reflections with $(h+k+l)/2$ odd.

$$f(K) \equiv f(hkl) = \langle j_0(K) \rangle + \epsilon\,(2{\cdot}5\,A(hkl))\,\langle j_4(K) \rangle \tag{3}$$

$$A(hkl) = \frac{h^4+k^4+l^4-3(h^2k^2+k^2l^2+h^2l^2)}{(h^2+k^2+l^2)^2} \tag{4}$$

$$\langle jn(K) \rangle = \int_0^\infty jn(Kr)\, R^2(r)\, r^2\, dr \tag{5}$$

$$K = 4\pi \sin \theta/\lambda \tag{6}$$

ϵ represents the excess of population of unpaired $3d$ electrons in E_g orbitals, i.e. the fractional populations in E_g and T_{2g} states respectively are $(\epsilon+0{\cdot}4)$ and $(0{\cdot}6-\epsilon)$. The j_n's are the spherical Bessel functions. The Bessel radial integrals $\langle j_0(K) \rangle$ and $\langle j_4(K) \rangle$ appropriate to Mn^{2+} ions were used in the analysis. $R(r)$ is the radial part of $3d$ electron wave function.

For the purpose of refinement a single value of γ for each reflection was arrived at from consideration of confidence in individual measurements or by averaging the set of γ-values for any reflection. The weights for the observations were taken as the inverse square of estimated errors. The nuclear parameters were taken as deduced from unpolarised neutron measurements. Moments on all the three sites, as well as the asymmetry parameter ϵ were varied. The results are summarised below. The

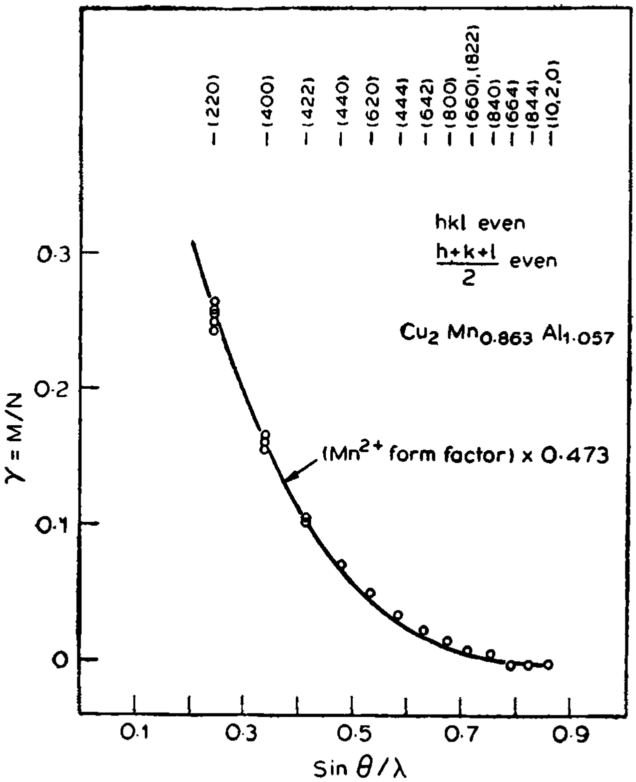

Figure 2 (c). Even reflections with $(h+k+l)/2$ even. Scaled Mn^{2+} free ion form factor is plotted for comparison in each case.

net total localised moment per formula unit as obtained from the refined moment values is also shown.

$$\begin{aligned} \langle\mu_{Cu}\rangle &= 0{\cdot}03 \pm 0{\cdot}02 \quad \mu_B \\ \langle\mu_{Al}\rangle &= -0{\cdot}06 \pm 0{\cdot}03 \quad \mu_B \\ \langle\mu_{Mn}\rangle &= 2{\cdot}87 \pm 0{\cdot}05 \quad \mu_B \\ \epsilon &= 0{\cdot}035 \pm 0{\cdot}006 \\ \text{Net local moment} &= 2{\cdot}87 \pm 0{\cdot}13 \quad \mu_B. \end{aligned} \tag{7}$$

The net localised moment value of 2·87 μ_B is very close to the saturation magnetisation value of 2·89 μ_B per formula unit at room temperature. This shows that the diffuse conduction electron polarisation in the sample, if any, is small. The moment on each Mn atom can be calculated from the known composition of the sample to be 3·3 μ_B.

Table 2. Experimental magnetic structure amplitudes compared with the values calculated from refined parameters. The estimated fractional error on γ is also shown.

Reflection type	*hkl*	*M*(*hkl*) (obs)	*M*(*hkl*) (calc)	Fractional error on $\gamma = (M/N)$
I	111	2·478	2·514	0·08
	311	1·492	1·470	0·02
	331	0·905	0·912	0·01
	333	0·596	0·583	0·02
	511	0·598	0·607	0·01
	531	0·410	0·391	0·02
	533	0·250	0·250	0·04
	711	0·188	0·190	0·05
	551	0·151	0·163	0·05
	553	0·099	0·095	0·09
	731	0·128	0·115	0·07
	733	0·065	0·062	0·18
	751	0·037	0·028	0·24
	555	0·030	0·015	0·44
	753	0·001	0·000	5·10
	911	0·036	0·031	0·39
	755	−0·038	−0·033	0·25
	771	−0·017	−0·025	1·30
	933	0·011	−0·014	0·70
	951	−0·023	−0·026	0·46
II	200	2·186	2·183	0·01
	222	1·216	1·268	0·01
	420	0·788	0·793	0·01
	600	0·359	0·357	0·02
	442	0·345	0·323	0·02
	622	0·238	0·222	0·05
	640	0·139	0·137	0·08
	644	0·044	0·033	0·23
	820	0·058	0·065	0·22
	662	0·008	0·011	1·25
	842	0·007	0·002	1·01
	860	−0·037	−0·027	0·51
	10,0,0	0·002	0·001	1·00
III	220	1·659	1·734	0·01
	400	1·012	1·070	0·02
	422	0·646	0·671	0·02
	440	0·441	0·437	0·02
	620	0·319	0·305	0·03
	444	0·212	0·175	0·06
	642	0·147	0·116	0·08
	800	0·093	0·099	0·11
	660	0·050	0·033	0·30
	822	0·058	0·051	0·21
	840	0·025	0·019	1·52
	664	−0·021	−0·018	0·52
	844	−0·021	−0·022	0·83
	10,2,0	−0·016	−0·006	0·71

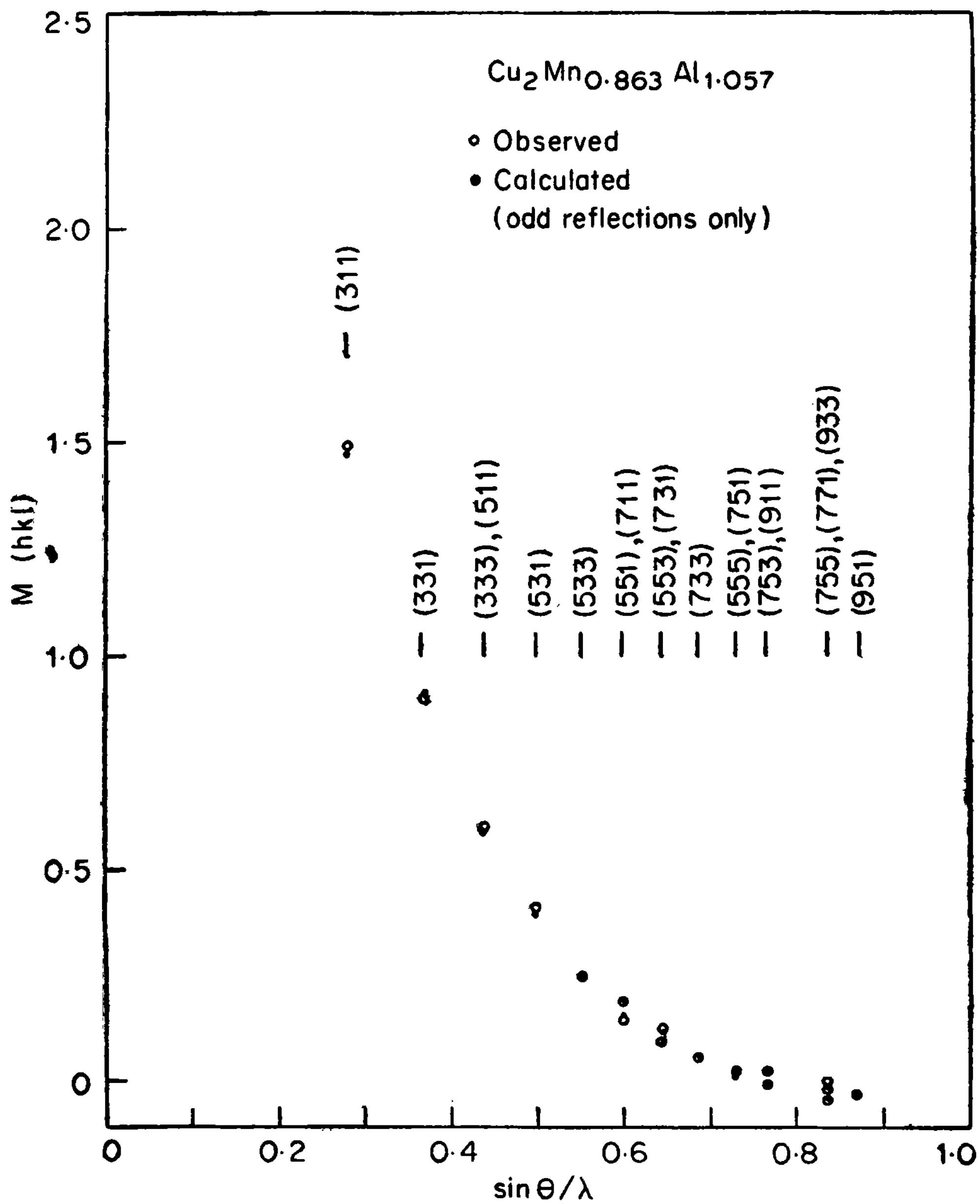

Figure 3. Comparison of observed and calculated (fitted) *M*-values for odd reflections.

3.4. *Comparison of calculated and observed M-values*

In table 2 we compare the calculated (from fitted parameters) and the observed values of magnetic structure amplitudes for all reflections except (111) which was excluded from refinement because of its large sensitivity to the depolarisation correction. *M*(obs) and *M*(calc) are obtained by

Table 3. Comparison of observed and calculated difference in M-values of pair of reflections with the same Bragg angle.

Sl. No.	$h_1k_1l_1$	$h_2k_2l_2$	M_1-M_2 (calc)	M_1-M_2 (obs)
1	333	511	−0·024	−0·002
2	711	551	+0·027	+0·037
3	553	731	−0·020	−0·029
4	751	555	+0·013	+0·007
5	753	911	−0·031	−0·035
6	755	771	−0·008	−0·021
7	771	933	−0·011	−0·028
8	755	933	−0·019	−0·049
9	600	442	+0·034	+0·014
10	644	820	−0·032	−0·014
11	860	10, 0, 0	−0·028	−0·039
12	660	822	−0·018	−0·008

$M_1=M(h_1k_1l_1)$, $M_2 = M(h_2k_2l_2)$

$$M\,(\text{obs}) = \gamma\,(\text{obs}) \times N(hkl)$$

$$M(\text{calc}) = \gamma\,(\text{calc}) \times N(hkl)$$

We plot in figure 3 these values for the odd reflections only. The agreement between the observed and the calculated values is seen to be good.

The differences in the M values of pairs of reflections at the same angle, both calculated and observed are shown in table 3. The two agree in sign in all cases though not in magnitude. This analysis thus shows that there is a small asphericity present in the moment distribution contrary to the conclusion of Takata (1965). The estimated populations of electrons in the E_g and T_{2g} orbitals are: E_g : 43·5 %, T_{2g} : 56·5 % as shown in the previous section.

4. Conclusions

(i) The magnetic moment in Cu_2MnAl is principally due to Mn atoms and the corresponding form factor is like that of a Mn^{2+} free ion. A similar result was obtained by previous workers and also by Ishikawa *et al* (1976) in another Heusler alloy Pd_2MnSn. The moment on each Mn is determined to be $3{\cdot}3\mu_B$. The present sample is deficient in Mn but this apparently has no appreciable effect on the Mn moment when compared with the value of $3{\cdot}2\mu_B$ in fully stoichiometric samples (Takata 1965; Felcher *et al* 1963). The value obtained by Forsyth (1963) is apparently lower.

(ii) A small asphericity in the magnetic moment density on Mn sites has been inferred from the present study for the first time, which is consistent with about 3 % excess of $3d$ electrons in E_g states ($d_{x^2-y^2}$, d_{z^2}) as compared to the spherical distribution ($E_g : T_{2g} = 2:3$).

(iii) There is some evidence from the least squares refinement of M/N values that Cu sites have a slight *positive* moment. The magnitude, however, is extremely small and subject to an error of $\sim 0{\cdot}1\mu_B$. Ishikawa *et al* (1976) had observed a small polarisation of Pd ions in Pd_2MnSn and had suggested a larger polarisation for the Cu ions in Cu_2MnAl (Kasuya 1974). This expectation is thus not realised.

(iv) The diffuse conduction electron polarisation, if any, is very small since the total localised moment is very close to the saturation magnetisation value of $2{\cdot}89\mu_B$ per formula unit. Consideration of small extinction in the sample showed that the deduced value of local moment could be somewhat larger and thus the conduction electron polarisation may be small and negative.

List of symbols

b_ν	nuclear scattering amplitude of nucleus at site ν
p_ν	magnetic scattering amplitude for site ν
μ_ν	magnetic moment at site ν in Bohr magnetons
μ_B	Bohr magneton
N	or $N(hkl)$ is the nuclear structure amplitude for reflection (hkl)
M	or $M(hkl)$ is the magnetic structure amplitude for reflection (hkl)
γ	$\gamma = M/N$
θ	Bragg angle
λ	neutron wavelength
P	netron beam polarisation
f	flipping efficiency of r.f. flipper
K	momentum transfer $= 4\pi \sin\theta/\lambda$
$e^{-2B(\sin\theta/\lambda)^2}$	Debye-Waller factor
B	temperature factor
$f(K)$, $f(hkl)$	magnetic form factor
ϵ	asphericity parameter for moment density of Mn ($\epsilon = 0$ for spherica symmetry)
j_n	spherical Bessel function of order n

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