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An investigation of the atomic and magnetic structure of mechanically alloyed Cu₂MnAl using neutron diffraction and the Rietveld method

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Abstract. The Heusler alloy Cu₂MnAl was prepared by mechanical alloying and subsequent heat treatment at 973 K for 1 h. At saturation, the resulting material had an atomic magnetic moment of 2.34 μ_B /Mn atom. Neutron diffraction experiments were carried out at room temperature, both with and without an applied magnetic field of 12 kOe. The Rietveld method was used to fit calculated curves to both sets of data. Nuclear and magnetic contributions were modelled simultaneously, using a large Debye–Waller thermal parameter to model the Mn²⁺ magnetic form factor. The results showed that the material was ferromagnetic. Cu atoms occupied approximately 10% of the Mn sites. Particle and magnetic domain sizes were determined from the results of the Rietveld analysis. These were respectively ~ 164 and ~ 29 nm. The nuclear contribution to the diffraction pattern was separated from the magnetic, by subtraction of the two sets of data. This was studied using the Rietveld method and the resulting structure was similar to that obtained when nuclear and magnetic components were modelled simultaneously.

1. Introduction

It has been shown [1] that when pure Cu, Mn and Al powders are mechanically alloyed a highly disordered nanocrystalline Cu₂MnAl compound can be formed. Heat treatment at 973 K results in a material that is highly ferromagnetic. X-ray diffraction and magnetic measurement techniques have shown that the structure is similar to that previously reported for conventionally prepared Cu₂MnAl [2–4], with the exception that the mechanically alloyed material has a smaller crystallite size.

The Heusler structure is illustrated in figure 1. The structure is face centred cubic, having space group $Fm\bar{3}m$. There are four Cu₂MnAl molecules per unit cell. Cu atoms reside at $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$, Mn at $(1/2, 1/2, 1/2)$ and Al at $(0, 0, 0)$ [5]. A neutron diffraction study by Felcher *et al* [6] established that the magnetic moment in Cu₂MnAl can be solely attributed to the Mn atoms. It has been shown [7] that there is no significant direct interaction between the magnetic moments, since, when located at $(1/2, 1/2, 1/2)$ positions within the Heusler structure, the separation of Mn atoms is too large. Indirect exchange mechanisms of the RKKY type have been used to describe the coupling of moments by way of the conduction electrons [7–9]. Since the magnetic properties of Cu₂MnAl are directly related to atomic structure, any factor affecting chemical order will directly influence magnetic behaviour [10].

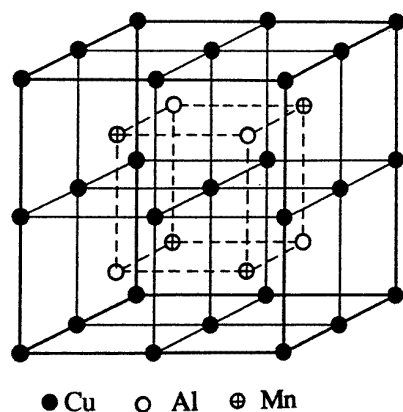


Figure 1. The stoichiometric Cu_2MnAl unit cell, showing the four interpenetrating FCC sublattices. Cu atoms occupy $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$ positions. Mn atoms are at $(1/2, 1/2, 1/2)$ and Al at $(0, 0, 0)$.

Neutron diffraction has the advantage over the more conventional x-ray diffraction, in that nuclear scattering amplitudes are not dependent upon atomic number. Elements such as Cu and Mn, which are close together in the periodic table, can easily be distinguished [11]. Since neutrons are also scattered magnetically, it is possible to assess the state of magnetic order within a material. The Rietveld method has been extensively utilized in the solution of powder diffraction patterns [11]. This is a computer based concept which allows least-squares fitting of a calculated curve to the diffraction data points. This is achieved by variation of thermal parameters and structure factors based upon the various combinations of atomic site occupancy [12–14]. In the Rietveld code used in the present analysis [15], a number of phases can be modelled simultaneously. A scale factor is refined for each, which relates to the number of unit cells of a particular phase present in the sample [14]. It is assumed that the line broadening caused by small reflecting domains is Lorentzian. A Lorentzian width parameter is refined during the analysis; this can be related to the Scherrer equation in order to determine the particle size of each phase included in the refinement [14]. Agreement indices provided by the Rietveld output are used to assess the completeness of the refinement. Of these, the profile $R(R_p)$ and weighted profile $R(R_{wp})$ indices relate to the differences between the observed data points and those calculated during the Rietveld analysis. The Bragg $R(R_B)$ index gives an indication of the differences between the integrated intensities of the observed and calculated Bragg reflections. In each case, a lower value indicates a superior refinement [13, 14].

Traditionally, before analysis of an ordered magnetic material can proceed, the nuclear and magnetic contributions to the neutron diffraction pattern are separated. This can be achieved by comparison of data collected either with and without an applied magnetic field or above and below the magnetic ordering temperature, both of which serve to alter the intensities of magnetic reflections. In the present study, the Rietveld method has been used to model these contributions simultaneously. In order to check the results, the nuclear component was separated by the use of an applied magnetic field and modelled independently.

When neutron diffraction measurements are made on a demagnetized ferromagnet, the

resulting structure factors of the individual Bragg reflections are given by equation (1a) below. F_{nuc} and F_{mag} refer respectively to the structure factors of the nuclear and magnetic components. In the case of a ferromagnet which is saturated in a direction perpendicular to the scattering vector, the structure factors are given by equation (1b) [16].

$$F_{(hkl)}^2 = F_{nuc}^2 + \frac{2}{3}F_{mag}^2 \quad (1a)$$

$$F_{(hkl)}^2 = F_{nuc}^2 + F_{mag}^2 \quad (1b)$$

Subtraction of the ‘field off’ data from the ‘field on’ data hence results in reflections which are equivalent to one-third of the magnetic intensities.

2. Experimental procedure

In order to produce the volume of material required for a neutron diffraction experiment, the sample used in the present study was prepared by mechanically alloying high-purity Cu, Mn and Al powders under an argon atmosphere for 23 h in a Fritsch Pulvisette 5 planetary ball mill, at an indicated rotational speed of 340 rpm. A hardened steel vial with an internal diameter of 105 mm was used. The balls were also hardened steel, used at a ball:powder ratio of 16:1. The resulting powder was compacted into a number of 12 mm diameter cylinders. During the experiments, these were stacked one upon the other. The total height was 39 mm. The cylinders were first vacuum sealed in Vycor tubing and heat treated for 1 h at 973 K. Magnetic measurements were conducted at room temperature, using an Oxford Instruments vibrating sample magnetometer. A 5 mm diameter cylinder was prepared for this purpose. The neutron diffraction experiments were conducted using the medium-resolution neutron powder diffractometer (MRPD) [17] at the HIFAR research reactor at Lucas Heights Research Laboratories, NSW. The wavelength of the neutron beam was 1.664 Å. Measurements were made both with and without an external magnetic field of approximately 12 kOe acting on the specimen. The field was applied in a direction perpendicular to the scattering vector by means of an electromagnet. The data were collected over periods of 7.5 and 15 h respectively.

3. Results

Chemical analysis showed that the as-milled material was deficient in Mn and Al, with an indicative composition $\text{Cu}_{2.00}\text{Mn}_{0.93}\text{Al}_{0.96}$. A magnetization curve, measured after heat treatment, is shown in figure 2. The material had a saturation magnetization of 62 emu g^{-1} , corresponding to an atomic magnetic moment of 2.34 μ_B/Mn atom. The room-temperature magnetic moment reported previously in Cu_2MnAl alloys was approximately 3 μ_B/Mn atom [1–4, 17].

The neutron diffraction pattern collected in zero applied magnetic field, with Rietveld fitted curve, is shown in figure 3. The refinement was achieved by modelling the nuclear and magnetic components as two separate phases. The magnetic phase was input as Mn atoms at the (1/2, 1/2, 1/2) positions of an $Fm\bar{3}m$ structure. The magnetic form factor was taken into account by allowing the thermal parameter of the magnetic phase to exceed that of the Mn atoms in the nuclear phase by ten. The justification for this approximation is dealt with in section 4. The agreement indices for the Rietveld refinement, R_p and R_{wp} , along with the R_B indices for the nuclear and magnetic components, appear in table 1.

The lattice constant determined by the refinement was 5.950 Å. In addition to the expected FCC reflections in the diffraction pattern, there were five additional low-intensity

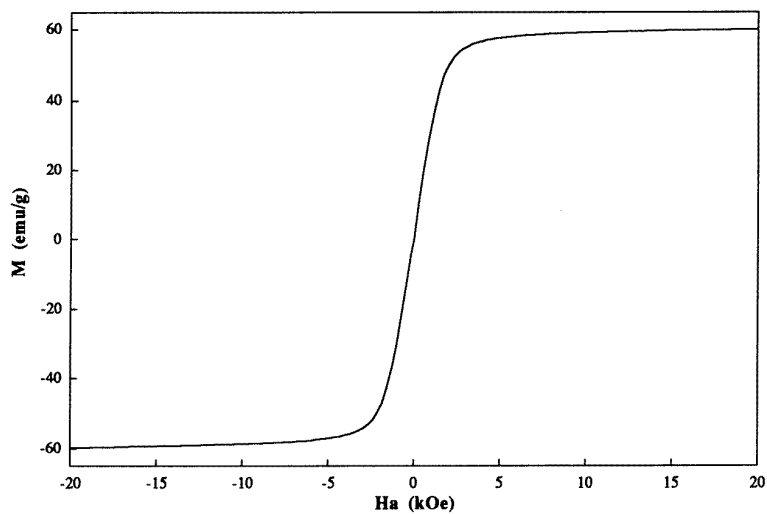


Figure 2. Magnetization curve of mechanically alloyed Cu₂MnAl, performed at room temperature, after heat treatment for 1 h at 973 K.

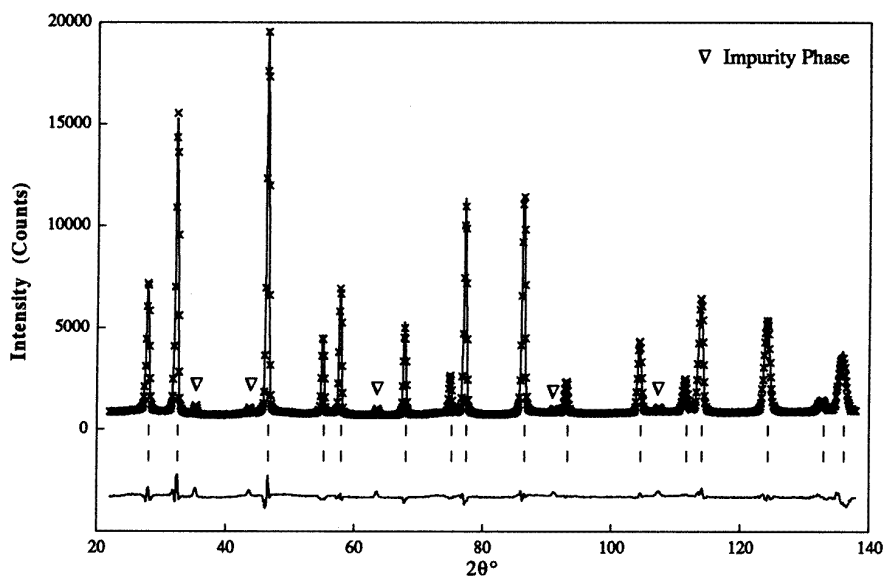


Figure 3. Rietveld refinement of mechanically alloyed Cu₂MnAl, heat treated for 1 h at 973 K. The crosses represent the data points, the solid line fitted to these is the calculated curve. Beneath are shown the difference plot and the markers for the expected locations of nuclear and magnetic peaks.

reflections, presumably associated with an impurity phase. It has not been possible to identify this phase and it was not included in the refinement. The particle size (crystallite

Table 1. Refinement indices generated by Rietveld analyses of experiments conducted under 'field off' and 'field on' conditions and the analysis of the separated nuclear component.

Details	R_p (%)	R_{wp} (%)	R_B (%)	
			nuclear phase	magnetic phase
Field off	4.58	5.86	2.28	1.83
Field on	4.89	6.14	2.01	1.78
Nuclear component	5.15	6.55	3.15	—

size) of the nuclear phase and the magnetic domain size were respectively 166 and 29 nm.

The scale factors from the Rietveld analysis relating to the nuclear and magnetic phases were compared. These, along with the known value of the nuclear scattering length of Mn and a correction for the incomplete occupancy of the Mn sites, were used to determine the magnetic moment associated with each Mn atom as $2.15 \mu_B$. The uncertainty associated with this value was 6.2%, resulting from the cumulative statistical uncertainty of variables indicated by the Rietveld output.

Table 2. Composition, magnetic moment and particle sizes of the nuclear and magnetic components, resulting from the Rietveld analyses of the indicated diffraction curves. Compare to chemical analysis, $\text{Cu}_{2.00}\text{Mn}_{0.93}\text{Al}_{0.96}$, and magnetization measurements, $2.3 \mu_B$.

Details	$\text{Cu}_x\text{Mn}_y\text{Al}_z$			μ (μ_B)	Particle size (nm)	Magnetic domain size (nm)
	X	Y	Z			
Field off	2.12(± 0.004)	0.88(± 0.004)	1.00	2.15(± 0.13)	166	29
Field on	2.12(± 0.004)	0.88(± 0.004)	1.00	2.12(± 0.12)	162	41
Nuclear component	2.11(± 0.015)	0.91(± 0.003)	0.99(± 0.012)		138	

The pattern collected with a magnetic field applied to the specimen was examined in a similar way. The agreement indices are given in table 1 and the particle size, domain size and calculated moment are shown in table 2. Results of both 'field on' and 'field off' refinements showed that all Cu atomic sites were occupied by Cu atoms. A stable refinement was achieved by assuming that the Al sites were also filled. The Mn site occupancy fraction was less than one, indicating that, in addition to Mn atoms, either Cu or Al atoms or vacancies were present on the Mn sublattice. Since the chemical analysis had shown that there was an excess of Cu atoms in the alloy and the Al sublattice appeared to be filled with Al atoms, it was assumed that the excess Cu atoms occupied Mn sites. The overall indicative composition was $\text{Cu}_{2.12}\text{Mn}_{0.88}\text{Al}_{1.00}$. The Rietveld output indicated that there was an uncertainty of 0.5% associated with the Mn content given by this formula. The composition has been expressed in this way to highlight the occupancies of the Mn and Al sites. When normalized for comparison with the chemical analysis, the result was $\text{Cu}_{2.00}\text{Mn}_{0.83}\text{Al}_{0.94}$.

The results plotted in figure 2 show that the field of 12 kOe applied to the sample in the neutron diffraction experiments was sufficient to saturate the sample. Thus equations (1a) and (1b) may be used directly to separate the nuclear and magnetic components of the diffraction pattern. The resulting magnetic diffraction pattern is shown in figure 4. The associated nuclear diffraction pattern with Rietveld fitted curve is shown in figure 5. The agreement indices associated with this are shown in table 1. The Cu atomic sites again

appeared to be filled with Cu atoms and the Mn occupancy fraction was less than one, but, in this case, a stable refinement was achieved with an incomplete Al site occupancy. Comparison of scattering lengths was consistent with the assumption that Cu atoms were present on the Al sublattice. The resulting composition and particle size are shown in table 2.

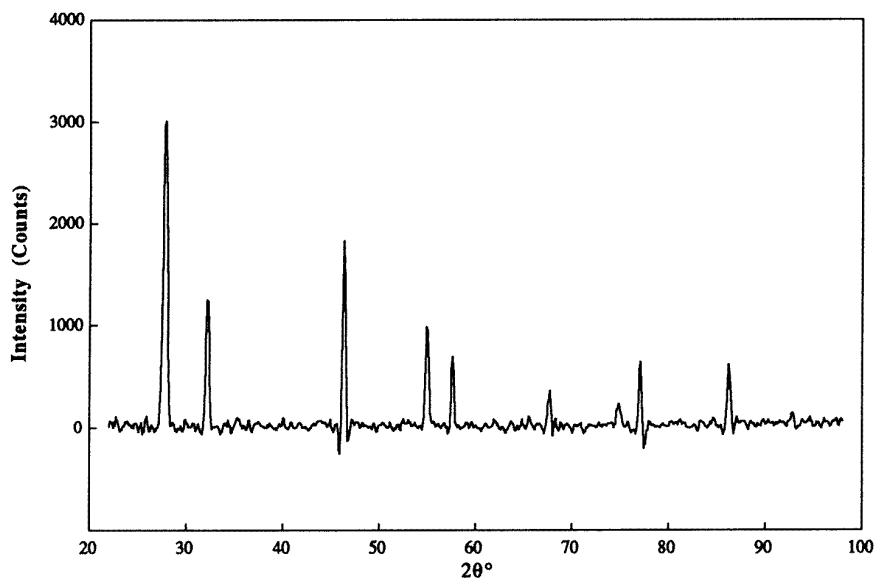


Figure 4. The magnetic diffraction pattern generated by subtraction of the 'field off' curve from the 'field on' curve.

4. Discussion

Previously, the saturation magnetization of Cu_2MnAl , mechanically alloyed using a Spex 8000 mixer/mill, was approximately 80 emu g^{-1} at room temperature after heat treatment at 973 K. This corresponds to $\sim 3.01 \mu_B/\text{Mn atom}$ [1]. Reported values of M_s in conventionally prepared alloys vary from $\sim 75 \text{ emu g}^{-1}$ [4, 17] to $\sim 90 \text{ emu g}^{-1}$ [2, 3]. The material used in the present study has $M_s = 62 \text{ emu g}^{-1}$ only. The observed differences in saturation magnetization are due to differences in chemical composition. The larger surface area of the vial used in the present study complicated the phenomenon described in [1] whereby the vial walls become coated with reactants during milling, changing the resulting composition. The magnetic properties of this alloy are particularly sensitive to composition. Heusler's experimental results given in [18] show that any departure from the ideal composition of Cu_2MnAl results in a decrease in the measured magnetization.

Comparison of figures 4 and 5 clearly shows that the angular positions of the magnetic and nuclear reflections coincide. This confirms that magnetic moments are coupled ferromagnetically in this material. It is hence justifiable to use Mn atoms located at the usual Mn sites in the Heusler structure to model the magnetic phase in the Rietveld refinement. It was shown by Takata [19] using polarized neutron diffraction techniques, that the measured

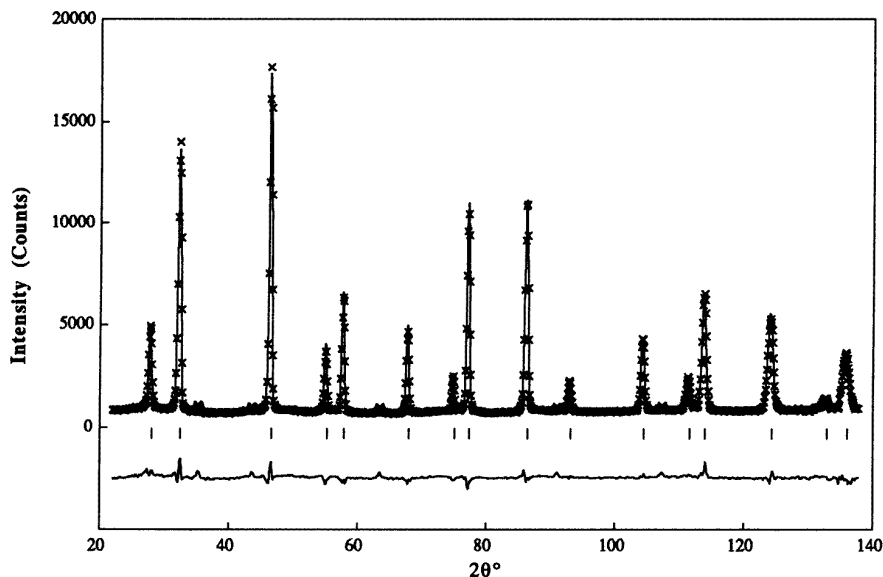


Figure 5. Rietveld refinement of the separated nuclear diffraction curve.

magnetic form factor of Cu_2MnAl corresponded to the calculated Mn^{2+} spherical form factor. This is shown plotted against $\sin\theta/\lambda$ in figure 6.

$$\text{Debye-Waller factor} = e^{-w} \quad w = B \left(\frac{\sin\theta}{\lambda} \right)^2. \quad (2)$$

Equation (2) shows the temperature dependent Debye-Waller factor which is used in the calculation of the structure factors in the Rietveld program [15]. A least-squares fit of the thermal parameter (B) to the calculated Mn^{2+} magnetic form factor [20] returned a value of ten. The two factors are shown, plotted against $\sin\theta/\lambda$, in figure 6. Using the present Rietveld analysis program, in order to account for the magnetic form factor, the Mn thermal parameter of the magnetic phase was set to exceed the Mn parameter of the nuclear phase by ten. It can be seen from figure 4 that the intensities of the magnetic reflections are significant up to $2\theta \sim 85^\circ$, which corresponds to $\sin\theta/\lambda \sim 0.4 \text{ \AA}^{-1}$. The discrepancy between the chosen thermal parameter and the calculated Mn^{2+} form factor at this level is approximately 14%. It is however the more intense reflections at lower angles which play a major role in the determination of the magnetic moment. The two parameters generally agree to within 2% in this region. This corresponds to an error of less than $\sim 4\%$ in the calculations, since the square of the form factor is used.

The chemical composition determined from the results of modelling nuclear and magnetic components simultaneously is, within the limits of experimentation, essentially equivalent to that obtained when the nuclear scattering was modelled separately. The composition determined by chemical analysis differs from this by ~ 10 and $\sim 2\%$ regarding Mn and Al content respectively. The magnetic moment determined from the measurement of saturation magnetization differed from those resulting from the refinement by $\sim 9\%$. In addition to the statistical uncertainties quoted in table 2 and the error introduced by the approximation of the magnetic form factor, another possible source of discrepancy is the

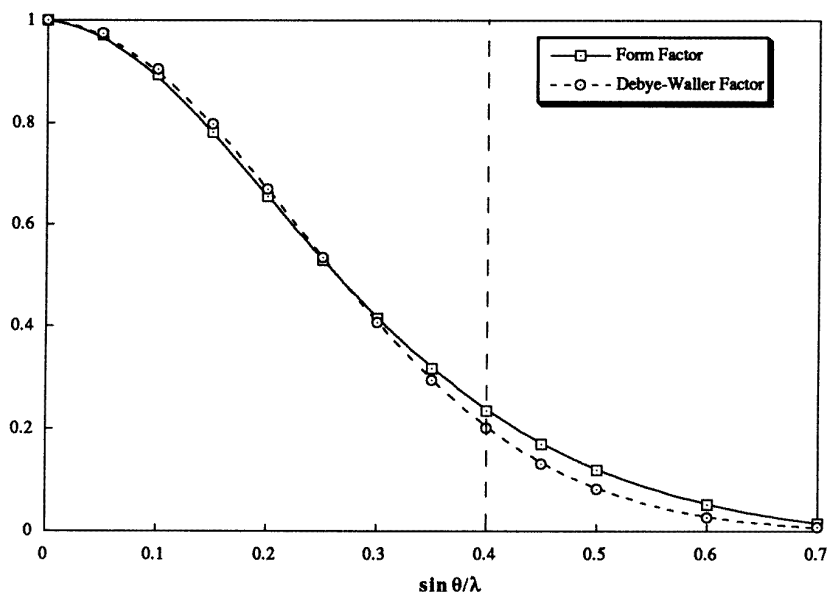


Figure 6. The Debye–Waller thermal parameter ($B = 10$) used to model the Mn^{2+} magnetic form factor in the Rietveld refinements, compared to the calculated form factor, after Watson and Freeman [20]. Dotted vertical line indicates the position of the highest-angle magnetic reflection observed in figure 4.

impurity phase evident in the diffraction curves. This was not included in the model. If this phase were rich in Mn, then this would explain why the suggested Mn content of the Heusler phase is reduced. The relative concentrations indicated by the Rietveld method refer specifically to the Heusler phase, whereas the chemical analysis gives only the overall concentrations. Since the intensities of the impurity peaks remained unchanged after the magnetic field was applied, it can be concluded that the impurity was not ferromagnetic, which eliminates this as a source of error when comparing measured and calculated magnetic moments.

Comparison of the two values of magnetic domain size in table 2 shows that the application of the magnetic field caused a narrowing of the magnetic peaks, since the suggested domain size was larger, indicated by a smaller Lorentzian component. Close examination of figure 4 supports this, since there are negative wings evident in some of the magnetic peaks, obtained by subtraction of the ‘field off’ curve from the ‘field on’ curve. In an ideal particulate system, the dimensions of the magnetic domains should be equal to those of the crystallites when saturated. The results in table 2 show a significant difference in these dimensions, due to the effects of the non-stoichiometric composition of the sample.

The particle sizes resulting from the two refinements in which the nuclear and magnetic phases were modelled simultaneously are similar. The average of these is 164 nm. The value obtained from the refinement of the separated nuclear scattering is somewhat lower. This is thought to be less accurate, since the strongest indication of particle size is contained within the bases of the diffraction peaks. The shapes of these are sensitive to inaccuracies introduced by the subtraction of the ‘field off’ curve from the ‘field on’ curve. Particle sizes can be determined by conducting transmission electron microscopy (TEM) studies. TEM

studies have not been conducted on the present material processed in the planetary ball mill. However, TEM analysis of Cu_2MnAl prepared using a Spex type mill, after heat treatment at 973 K for 5 min shows that the average particle size is approximately 160 nm, which is close to the results obtained for the present material, using the Rietveld method.

5. Conclusion

Neutron diffraction experiments were performed on a mechanically alloyed Cu_2MnAl Heusler alloy, which had been heat treated at 973 K. This was done both with and without an applied magnetic field. The Rietveld method was used to fit calculated curves to the diffraction patterns, modelling nuclear and magnetic components simultaneously. The Mn^{2+} magnetic form factor was accounted for by the use of a large thermal parameter. Nuclear and magnetic components were then separated and the nuclear component modelled independently. In both instances, the results indicated similar chemical compositions. The alloy contained an excess of Cu atoms and it was suggested that the majority occupy Mn sites with a small percentage of these on Al sites. Nuclear and magnetic phase scale factors were compared and the apparent atomic magnetic moment was calculated. The composition was also determined by chemical analysis and the moment was measured by using a vibrating sample magnetometer. The moment calculated using the Rietveld refinements differed from this by approximately 9%. The chemical composition determined by the refinements differed from the results of chemical analysis by approximately 10 and 2%, in Mn and Al content respectively. In addition to the uncertainties associated with each result, a small amount of an unknown impurity phase was detected in the diffraction patterns. This was not included in the Rietveld models and is hence a source of error. In addition, an error of up to $\sim 4\%$ in the scale factors arises from the approximation of the magnetic form factor. The average particle size of the nuclear component of the diffraction patterns was determined from the Rietveld analysis and was found to be ~ 164 nm. Similarly, the magnetic domain size was found to be 29 nm when the sample was in the demagnetized state. An increase to 41 nm was observed when the magnetic field was applied.

Acknowledgments

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