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Abstract

Neutron powder diffraction and magnetization measurements have been used to study the crystallographic and magnetic properties of $Ru_{2-x}Fe_xCrGe$ with $x = 0$, 1.0 and 1.7. Ru_2CrGe was found to have the Heusler $L2_1$ structure and to order antiferromagnetically below $T_N = 16.5$ K to a face centred cubic type 2 structure, propagation vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Only the Cr atoms carry a magnetic moment, which is oriented perpendicular to the propagation vector and has magnitude 1.45 μ_B at 5 K. Replacement of Ru by Fe causes the alloys to become ferromagnetic with accompanying disorder amongst the Fe, Cr and Ru atoms with only the Ge atoms remaining completely ordered. Both the neutron diffraction data and the magnetization results for the ferromagnetic alloys lead to non-integral values of the magnetic moment per formula unit differing significantly from the 2 μ_B predicted by band structure calculations. The materials can therefore not be expected to display ideal half metallic ferromagnetic properties.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Materials in which there is an energy gap at the Fermi level between the majority and minority spin bands are known as half metallic ferromagnets. Possible candidates are attracting considerable attention since their predicted properties are of both fundamental and technological interest. The presence of the band gap controls the transport properties and restricts the low temperature magnetic excitations to just spin waves, although with increasing temperature transitions across the gap between the majority and minority bands can occur. Such materials offer the possibility of exploiting the electron's spin in new semiconductor devices such as spin valves [1], as possible spin injector electrodes in tunnel magneto-resistance (TMR) structures [2, 3] or for spin polarized current injection into semiconductors (spintronics) [4]. Such devices require the injection of a spin polarized current and therefore substantial efforts are being made to find materials capable of providing such currents. The band structures calculated for a number of ferromagnetic compounds including Co_2MnSi [5], NiMnSb [6], CoS_2 [7], CrO_2 [8] have the necessary gap between the spin up and spin down bands. They might consequently have half metallic properties and be a potential source of spin polarized electrical currents.

Recent band structure calculations suggest that at some compositions the new Heusler alloy series $Ru_{2-x}Fe_xCrZ$ (Z = Si, Ge) should be ideal half metallic ferromagnets with a large density of states in the majority spin states at the Fermi level [9, 10]. The calculations predict an integral ground state moment of 2 μ_B almost independent of Fe concentration. It was in order to verify these predictions that the present study was undertaken.

2. Previous work

The first compound in which half metallic ferromagnetism was predicted to occur was NiMnSb [6]. NiMnSb has the non-centro-symmetric half Heusler $C1_b$ structure, space group $F\bar{4}3m$, derived from the Heusler structure $L2_1$ shown in figure 1 by emptying the (4d) $(\frac{3}{4}\frac{3}{4}\frac{3}{4})$ sites. Since this first prediction considerable effort has been expended searching for half metallic behaviour in isostructural compounds both by varying the constituent elements (XYZ) and by extending the composition range to include that of the full Heusler alloy (X_2YZ). As yet no ideal system has been found [11, 12].

The prediction on theoretical grounds of ideal half metallic ferromagnetism in $Ru_{2-x}Fe_xCrGe$ motivated a recent experimental study of a series of single phase alloys with
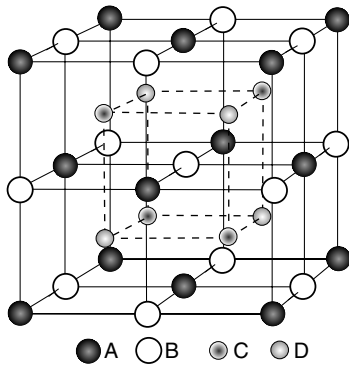
Figure 1. Positions of atomic sites in the cubic unit cell of structures derived from the L2$_1$ Heusler alloy. For the Heusler composition X$_2$YZ and space group $Fm3m$ the C and D sites belong to a single equivalent set 8(c) and are filled by the X atoms whilst the Y and Z atoms occupy the A and B sites, respectively. At the half Heusler composition XYZ the space group is $F\bar{4}3m$, the C: 4(c) and D: 4(d) sites are independent and the D sites are empty.
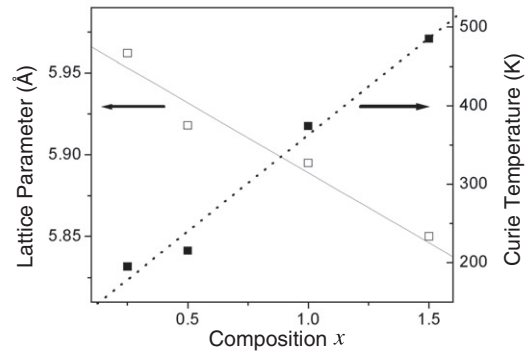

Figure 2. Lattice parameters and Curie temperatures of the ferromagnetic alloys in the series Ru$_{2-x}$Fe$_x$CrGe [13], plotted as a function of composition x.

$0.25 \leqslant x \leqslant 1.7$ [9, 10]. The linear decrease in lattice parameter with increasing x (figure 2) was taken to show that the Fe atoms enter the lattice sites randomly [13]. All the samples with $0.25 \leqslant x \leqslant 1.7$ were found to be ferromagnetic with Curie temperatures T_C increasing linearly with x as shown in figure 2. For the same range of composition the magnetic moment per formula unit derived from the saturation magnetization increased from 0.17 μ_B to 2.5 μ_B in contradiction with the theoretical prediction. The susceptibility of Ru$_2$CrGe on the other hand was found to remain essentially constant $\approx 1.4 \times 10^{-5}$ emu g^{-1} in the temperature range 4.5–350 K; the lack of ferromagnetic order in the pure phase was attributed by these authors [13] to possible atomic disorder or alternatively to antiferromagnetic coupling between Fe and Cr atoms.

In view of the conflict between the results of electronic structure calculations and the observed bulk properties, a neutron powder diffraction study of three alloys in the Ru$_{2-x}$Fe$_x$CrGe series: those with $x = 0$, 1.0 and 1.7 has been undertaken. Since the neutron scattering lengths of the constituent elements differ significantly (Ru 7.0 fm, Cr 3.63 fm, Ge 8.19 fm and Fe 9.45 fm) the results can be used to determine the degree of atomic order as well as the magnetic structures and magnetic moments.

3. Experimental details

3.1. Sample preparation

The powder specimens used in the experiments reported here: Ru$_{2-x}$Fe$_x$CrGe with $x = 0, 1.0$ and 1.7, came from the same ingots as the samples used in the earlier magnetization studies [13]. These ingots were prepared from spectrographically pure starting elements of 5N purity melted in an argon arc furnace. The ingots were crushed to form a powder with a particle size less than 250 μm which was sealed in quartz ampoules under a reduced argon atmosphere. Each powder was annealed for 5 days at 1000 °C

before being rapidly quenched in ice water. X-ray diffraction measurements made at room temperature showed that the specimens contained just a single phase which had the Heusler L2$_1$ structure.

3.2. Magnetization

Magnetization measurements were made using a SQUID magnetometer in fields up to 5.5 T and at stable temperatures between 5 and 350 K.

Initial measurements focussed on Ru$_2$CrGe which had previously been reported to be paramagnetic. The variation of its magnetization with temperature measured in a field of 0.1 T showed an anomaly in the vicinity of 16.5 K. Isotherms of magnetization measured at temperatures between 2 and 350 K led to the temperature dependence of susceptibility shown in figure 3. For temperatures below the peak at ≈ 10 K, the susceptibility increases with decreasing temperature indicating the presence of ferromagnetic correlations. The Arrott plots (M^2 versus B/M) at constant temperature were linear, as expected for isotropic magnets, but had negative intercepts on the M^2 axis. The intercepts on the B/M axis give the reciprocal susceptibility; their thermal variation suggests that below 16.5 K the compound orders antiferromagnetically. The plot of χ^{-1} versus temperature obtained from these isotherms is shown as an inset to figure 3(a). Above ≈ 20 K the susceptibility follows a Curie–Weiss law characterized by a paramagnetic Curie temperature of ≈ -494 K and a Curie constant of $22.5(4) \times 10^{-4}$ J T^{-2} kg^{-1} K^{-1} giving an effective paramagnetic moment of 2.42 μ_B/f.u. Assuming a gyromagnetic ratio $g = 2$ this leads to a spin value for Cr of 0.81 and a paramagnetic moment gS of 1.62 μ_B. The results of the magnetization measurements made on Ru$_{2-x}$Fe$_x$CrGe with $x = 1$ and 1.7 are shown in figure 4(a); they confirmed that at these compositions Ru$_{2-x}$Fe$_x$CrGe is ferromagnetic. For neither composition was the magnetic moment per formula unit found to be integral, nor did the thermal variation of the spontaneous magnetization follow the $J = 1$ Brillouin function shown in figure 4(b). A summary of the magnetic properties of the three alloys is given in table 1.
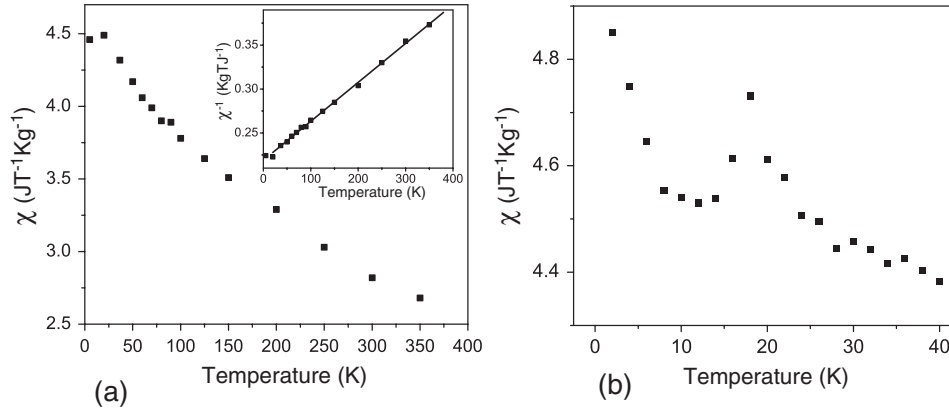
Figure 3. The uniform susceptibility of Ru_2CrGe (a) over the whole temperature range measured, (b) on a larger scale in the region below 40 K showing the anomaly associated with the onset of antiferromagnetic order at 16.5 K. The inset in (a) demonstrates the linear variation of the inverse susceptibility with temperature above 20 K.
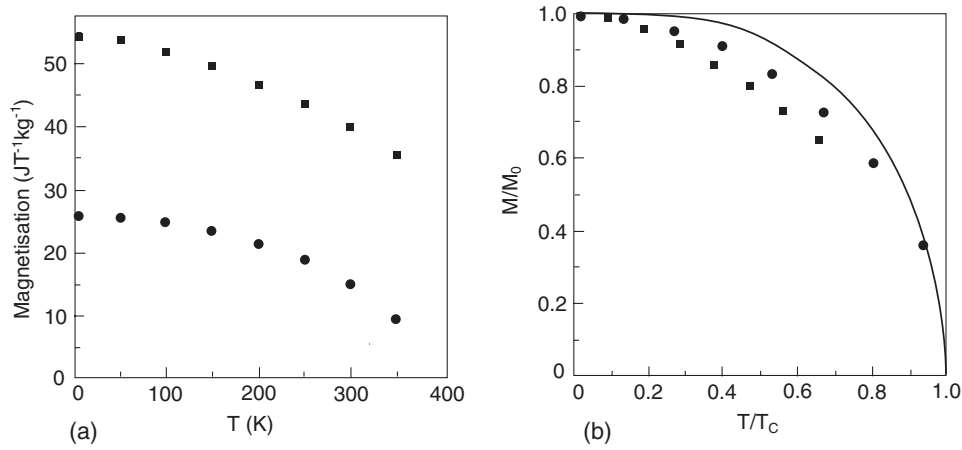

Figure 4. (a) The spontaneous magnetization of RuCrFeGe (filled circles) and $Ru_{0.3}Fe_{1.7}CrGe$ (filled squares), plotted against temperature. (b) The reduced magnetization as a function of reduced temperature for the two alloys compared to a $J = 1$ Brillouin function (full curve).

Table 1. Lattice constants and Magnetic properties of $Ru_{2-x}Fe_xCrGe$ alloys determined from magnetization and neutron diffraction measurements.

Alloy	a (Å)[a]	μ_0 (μ_B)[a]	T_C (K)[a]	T_N (K)[a]	P_{eff} (μ_B)[a]	μ_p (μ_B)[a]
Ru_2CrGe	5.970(5)			16.5(5)	2.42(4)	1.62(5)
RuFeCrGe	5.904(5)	1.30(4)	374[b]			
$Ru_{0.3}Fe_{1.7}CrGe$	5.857(5)	2.44(7)	533[b]			

[a] a is the lattice constant, μ_0 the magnetic moment per formula unit at 0 K, T_C the Curie temperature, T_N the Néel temperature, P_{eff} the effective paramagnetic moment and $\mu_p = gS$ the paramagnetic moment.
[b] From [13].

3.3. Neutron powder diffraction

Neutron powder diffraction patterns were obtained at temperatures, between 5 and 400 K using the high resolution neutron diffractometer D2b at the ILL in Grenoble. Using a neutron wavelength of 1.59 Å the intensity was recorded at 2θ values between 5 and 157° in steps of 0.05°. The powder sample were contained in thin walled vanadium tubes of diameter 5 mm located in an ILL 'orange cryofurnace' capable of providing temperatures stable to 0.2 °K over the required range. The diffraction patterns were analysed using the profile refinement technique as provided by the FullProf suite of programs [14]. The quality of the fits obtained in the profile refinements was measured using the 'goodness of fit' χ^2 defined by

$$\chi^2 = \sum [(I_{obs} - I_{calc})/\sigma I_{obs}]^2/(N_{obs} - N_{par})$$

where I_{obs} and I_{calc} are the observed and calculated intensities for the N_{obs} measured points, σI_{obs} is the estimated standard deviation of I_{obs} and N_{par} the number of fitted parameters.
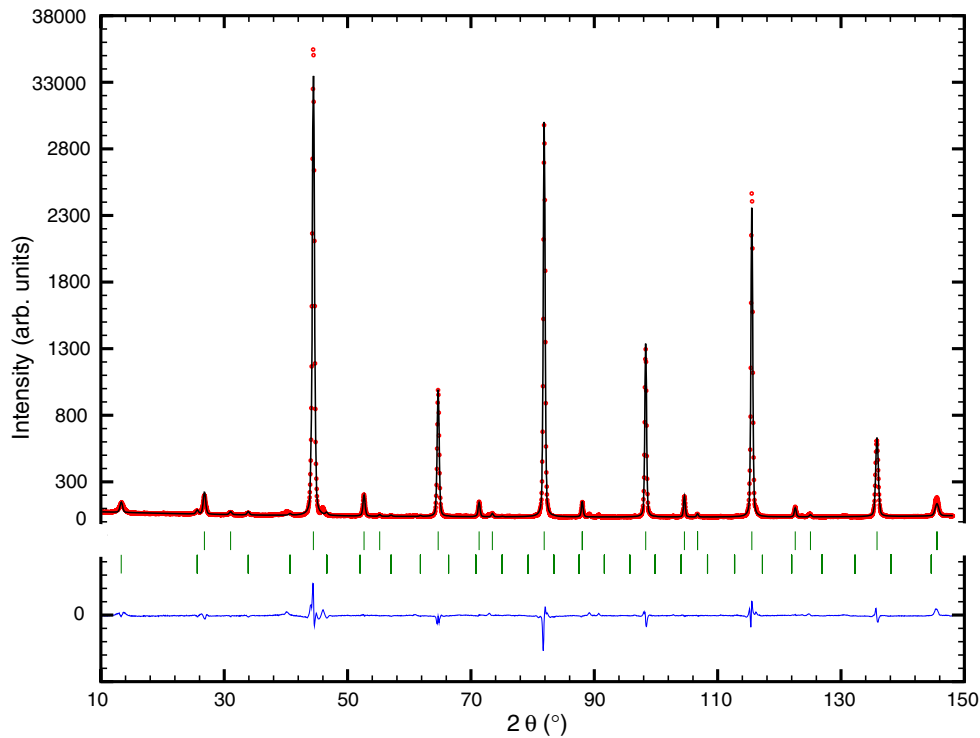
Figure 5. The observed and calculated neutron powder diffraction pattern of Ru_2CrGe in the paramagnetic phase. The lower curve shows the difference between the observed and calculated patterns. The upper and lower vertical tick marks give the positions of the nuclear and antiferromagnetic Bragg reflections, respectively.

4. Interpretation of the neutron diffraction results

4.1. Ru_2CrGe

The neutron powder diffraction pattern of Ru_2CrGe obtained in the paramagnetic phase at 400 K is shown in figure 5. Over the angular range covered in the experiment, $2° < 2\theta < 150°$, fourteen well defined Bragg peaks could be identified. They could all be indexed on a single fcc lattice confirming that the sample was single phase. Profile refinement of the diffracted intensities confirmed that, to within experimental error, the atoms were completely ordered in the Heusler $L2_1$ structure. No significant changes in the diffraction patterns were observed on cooling to 100 K, but below 16.5 K new peaks appeared, as shown in figure 6. Their wavevector dependence suggests that they are magnetic and they could be indexed on the cubic unit cell using a propagation vector $\tau = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. τ is parallel to the triad axis of the cubic unit cell so that the configurational symmetry is trigonal. Thus the antiferromagnetic structure has fcc type 2 order; the magnetic moments are ferromagnetically aligned within 111 planes with adjacent planes coupled antiferromagnetically as shown in figure 7. The presence of significant intensity in the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ magnetic Bragg peak shows that the magnetic moments are not parallel to the propagation vector. Profile refinement of the magnetic structure led to a moment of 1.45 μ_B per Cr atom aligned perpendicular to the propagation vector. The widths of the magnetic peaks were substantially greater than those calculated using the resolution function determined from the nuclear reflections. Assuming a Gaussian
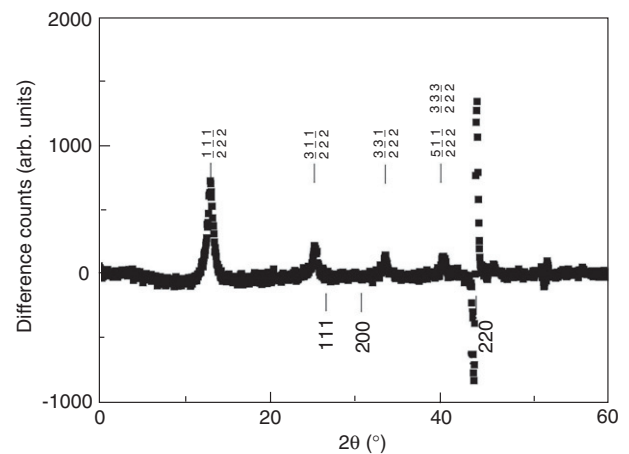

Figure 6. The difference between the patterns observed at 5 K and at 100 K showing the appearance of antiferromagnetic peaks at low temperature. The positions of the first three nuclear peaks (111), (200) and (220) are shown for comparison.

form for the instrumental resolution the intrinsic width of the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ magnetic peak was estimated to be 0.018 Å^{-1} leading to a magnetic correlation length of 350 Å. Refinements in which the Ru atoms were allowed to carry a magnetic moment gave substantially worse agreement. No change in shape or evidence of splitting in the high angle nuclear reflections could be observed on passing into the antiferromagnetic phase. Any associated magnetostriction is therefore small.

Table 2. Magnetic moments and site occupancies in the ferromagnetic alloys RuFeCrGe and $Ru_{0.3}Fe_{1.7}CrGe$. The site occupancies have been determined assuming the B sites contain only Ge and the high moment A site contains only Fe and Cr.

| | RuFeCrGe | | | $Ru_{0.3}Fe_{1.7}CrGe$ | | |
| | | Moment (μ_B) | | | Moment (μ_B) | |
Site	Occupancy	400 K	5 K	Occupancy	400 K	5 K
A	0.58Cr 0.42Fe		0.7(1)	0.33Cr 0.67Fe	0.76(10)	1.4(1)
B	Ge			Ge		
C	0.21Cr 0.29Fe0.5Ru		0.4(1)	0.39Cr 0.46Fe 0.15Ru	0.41(10)	0.7(1)
D	0.21Cr 0.29Fe0.5Ru		0.4(1)	0.28Cr 0.57Fe 0.15Ru	0.41(10)	0.7(1)
χ^2		4.8	3.8		7.7	7.3
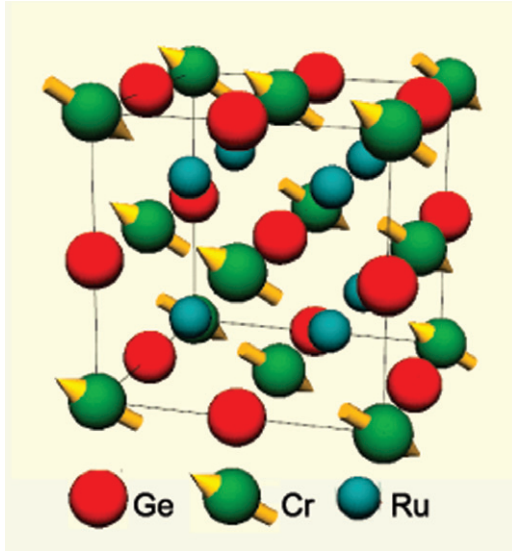
Figure 7. One octant of the antiferromagnetic unit cell of Ru_2CrGe showing the ordered arrangement of the Cr magnetic moments.

4.2. RuFeCrGe

At 400 K the diffraction pattern of RuFeCrGe is similar to that of Ru_2CrGe at the same temperature except that the reflections with h, k, l all odd are significantly weaker and those with $h + k + l = 4n + 2$ almost absent. A refinement carried out assuming that the Ru and Fe atoms occupy the C and D sites equally, with Cr and Ge ordered on the A and Ge on the A and C sites respectively, led to a substantial over-estimate of the intensities of the weaker reflections. For the Heusler alloy structure of figure 1 there are only 4 different structure factors:

h, k, l all even $h + k + l = 4n$

$$F = 4(b_A + b_B + b_C + b_D)$$

h, k, l all even $h + k + l = 4n + 2$

$$F = 4(b_A + b_B - b_C - b_D)$$

h, k, l all odd $h + k + l = 4n + 1$

$$F = 4(b_A - b_B) + 4\iota(b_C - b_D)$$

h, k, l all odd $h + k + l = 4n + 3$

$$F = 4(b_A - b_B) - 4\iota(b_C - b_D)$$

and since the last two are mutually complex conjugate, measurement of intensities yields only three independent equations for the four site scattering lengths. Only if it is assumed that the structure retains the Heusler type of ordering in which the C and D sites are equivalent can the site scattering lengths be determined independently. A refinement using this assumption gave $b_A = 6.1(3)$ $b_B = 8.2(2)$ and $b_{CD} = 7.0(4)$ fm. These scattering lengths are consistent with a structure in which the Ge atoms are fully ordered on the B sites and the Cr and Fe atoms almost equally distributed over the other three sites although with a slight preference of Cr for the A sites.

On cooling to 5 K the number and position of the Bragg peaks did not change. Furthermore the onset of ferromagnetic order led to only a small increase in the peak intensity of some of the low angle reflections. The intensity of the weak 200 reflection hardly changed whereas the 111 reflection, although small, almost doubled its intensity. However, compared with the nuclear component, the total magnetic scattering was very small. Since the B site contains only Ge atoms the refinement of the magnetic structure proceeded by establishing the moments on the other three sites consistent with the bulk magnetization. The values obtained in the refinement are given in table 2.

4.3. $Ru_{0.3}Fe_{1.7}CrGe$

At 400 K $Ru_{0.3}Fe_{1.7}CrGe$ is still in the ferromagnetic phase ($T_C = 533$ K), the diffraction pattern is similar to that of paramagnetic RuFeCrGe. Both the odd and even super-lattice reflections are very weak and are of similar intensity, much smaller than the fundamental $h + k + l = 4n$ reflections. An initial refinement of the nuclear structure using just the high angle reflections suggested that at this composition the structure is similar to that of the stoichiometric compound $x = 1$, except that there is an increased preference of the Fe atoms for the A sites. In subsequent refinements using the whole diffraction pattern the Ge atoms were confined to the B sites and moments were allowed on the A, C and D sites. The results of the refinement are given in table 2; the refined moments are in good agreement with the bulk magnetization. In the diffraction pattern of this alloy some small extra peaks were observed. They had intensities less than 1% of the fundamental reflections and could be indexed using a primitive cubic cell with $a \approx 4.6$ Å. There are three binary compounds with such a cell which can be formed from the four

constituent elements [16], namely Cr_3Ru, Cr_3Ge and Cr_3Fe but the additional peaks were not strong enough to allow positive identification of the contaminating phase.

Cooling to 5 K made very little change in the intensities of the fundamental reflections. However there were small but significant increases in the intensities of the weak low angle super-lattice peaks. The largest change was in the 111 reflection, which, like the same reflection in RuFeCrGe, essentially doubled in intensity on cooling. Refinement of the magnetic structure was again limited to determining the moments on the three transition metal sites (A, C and D). The results of the refinement are given in table 2 and the moments again agree well with bulk magnetization.

5. Discussion

The neutron diffraction measurements have established that below 16.5 K Ru_2CrGe orders antiferromagnetically with an fcc type 2 structure. For this structure the nearest neighbour exchange interactions at a distance of $a/\sqrt{2}$ are frustrated. However it is well established that, in Heusler alloys in which the magnetic moments are confined to the atoms on the A site, the magnetic exchange interactions have a very long range and may extend up to the seventh nearest neighbour [15]. Magnetic order occurs as a result of long range indirect exchange via the s–p conduction electrons and consequently the electron to atom ratio can have a profound effect on the type of magnetic order. It has also been suggested, on the basis of band structure calculations, that the magnetic moments per unit cell μ_0, in the ground states of Heusler alloys can be predicted from a modified Slater–Pauling curve: $\mu_0 = Z_t - 24$ where Z_t is the number of valence electrons [17]. This cannot however be applicable in the present case since both Ru and Fe come from the same column of the periodic table so Z_t does not change as Fe replaces Ru. The reason for the change in magnetic properties of $Ru_{2-x}Fe_xCrGe$ with increasing x, from antiferromagnetism to ferromagnetism must therefore be more subtle. The band structure calculations which predict half ferromagnetism with an integral moment of 2 μ_B were made for structures with $L2_1$ or $C1_b$ order, so may not be applicable a more disordered structure such as that found for $Ru_{2-x}Fe_xCrGe$. Assuming that the moment in the two ferromagnetic compounds is confined to the Fe atoms then from table 2 μ Fe = 1.3 and 1.44 μ_B for the compounds with $x = 1$ and 1.7 respectively.

In the antiferromagnetic phase of Ru_2CrGe the Cr atoms carry a moment of 1.45 μ_B and are separated in the $L2_1$ structure by 4.2 Å. Consequently as in other Heusler alloys in which the moment is confined to the A site atom, usually Mn, the compound may be considered to be a local moment system. Support for this classification comes from the near equality of the magnetic moments in the ordered and paramagnetic phases namely: 1.45 and 1.62 μ_B. Although Ru_2CrGe orders antiferromagnetically the widths of the magnetic diffraction peaks indicate that the ordered regions are of limited extent characterized by a correlation length of 350 Å. It is the thermal evolution of these correlations that gives rise to the upturn in the uniform susceptibility below 10 K.

Ferromagnetic properties similar to those found here for $Ru_{2-x}Fe_xCrGe$ have been reported [18] for the isoelectronic series $Ru_{2-x}Fe_xCrSi$, $0.5 \leqslant x \leqslant 1.8$. However for $0.5 \leqslant x \leqslant 1.5$ the alloys were reported to retain the $L2_1$ structure whereas for $x = 1.8$ a B2 structure was observed although the onset of B2 order did not appear to influence either the ground state moment, or the Curie temperature, significantly. For the $Ru_{2-x}Fe_xCrGe$ series Ru_2CrGe is highly ordered in the $L2_1$ structure and substitution of Ru by Fe leads to disorder of the Cr and Fe atoms amongst the A, C and D sites. With increasing x the Fe atoms increasingly populate all three of these sites and consequently the importance of direct exchange between Fe atoms increases. So long as the Ge atoms are confined to the B sites, the position usually found for a group V element in Heusler, the nearest neighbours of the A site are all transition elements. In both the ferromagnetic $Ru_{2-x}Fe_xCrGe$ alloys this site has the largest moment. The same is true of completely ordered $D0_3$ systems such as Fe_3Al and Fe_3Si in which the A site Fe moments are close to their elemental values. Further electronic structure calculations which take into account the disorder found here for alloys with $x = 1.0$ and 1.7 are required in order to clarify the predictions of half metallic behaviour in this series.

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