

## EXPERIMENTAL PROCEDURE

IV. 1 The Ni-Mn-Ge System

Alloys containing nickel, manganese and germanium have been reported by Pearson<sup>(21)</sup> to be composed of 4 different phases as follow:

(1)  $\text{Ni}_{1.3}\text{MnGe}_{0.7}$  has the hexagonal  $\text{MgZn}_2$  type structure,  $a = 4.856 \pm 2 \text{ \AA}$ ,  $c = 7.635 \pm 3 \text{ \AA}$ ,  $c/a = 1.572$

(2)  $\text{Ni}_{1.55}\text{MnGe}_{0.44}$  has the cubic  $\text{Cu}_2\text{Mg}$  type structure  $a = 6.762 \pm 1 \text{ \AA}$

(3)  $\text{Ni}_2\text{MnGe}$  has the cubic  $\text{Cu}_2\text{MnAl}$  type structure,  $a = 5.69 \text{ \AA}$

(4)  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$  has the cubic  $\text{Cu}_{16}\text{Mg}_6\text{Si}_7$  type structure,  $a = 11.41 \pm 1 \text{ \AA}$

Cerkasin et al<sup>(22)</sup> reported in 1957 that  $\text{Ni}_2\text{MnGe}$  has the cubic  $\text{Cu}_2\text{MnAl}$  type structure as quoted by Pearson.<sup>(21)</sup> Later in 1958 and 1962, as quoted by Kuz'ma et al<sup>(23)</sup>, Ni-Mn-Ge which

(22) Cerkasin, E.E., Gladyshevskij, E.I. and Kripjakevic, P.I., *Dopovidi ta povidomlenija, L'vivsk un-ta* 7 pt. 3 (1957) 180

(23) Kuz'ma, Ju.B., Tesljuk, M.Ju and Gladyshevskij, E.I., *J. Struct. Chem.*, 3 (1962) 143

(21) Pearson, W.B., Handbook of Lattice Spacings and Structures of metals, Volume 2, Pergamon Press, 1967

has the  $\text{Cu}_2\text{MnAl}$  type structure is given by a chemical formula  $\text{Ni}_x\text{Mn}_y\text{Ge}$  where  $x$  and  $y$  were not determined exactly. Therefore the composition of the Ni-Mn-Ge which give rise the  $\text{Cu}_2\text{MnAl}$  type structure may or may not be exactly the composition given by  $\text{Ni}_2\text{MnGe}$ . However, the atomic ratio must be close to the ratio 2:1:1, otherwise, the alloy must turn to other phases, either  $\text{Ni}_{1.3}\text{Mn}_{0.7}\text{Ge}$  or  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$  which have the atomic ratio 2:1.54:1.08 and 2:0.75:0.88 respectively.

#### IV. 2 Sample Preparation

The alloys were prepared from nickel 99.9%, manganese 99.95% and germanium 99.999% purity. Two samples of the same proportion of elements were prepared in different manners.

(1) The appropriate proportions of nickel, manganese and germanium with atomic ratio 2:1:1 were mixed together and melted in alumina crucible under argon atmosphere at  $1600^\circ\text{C}$ . After the initial melt the alloys were crushed to powder and remelted twice in order to ensure good mixing.

(2)  $\text{MnNi}$  and  $\text{NiGe}$  were first prepared by melting the right proportions of elements. The obtained ingots were crushed to powder, mixed together and remelted twice. All melting were in alumina crucibles under argon atmosphere and at  $1600^\circ\text{C}$ .

Neutron diffraction patterns of both samples reveal that the samples are double phase. The diffraction patterns can be indexed by two cubic structures corresponding to those of  $\text{Ni}_2\text{MnGe}$  and  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$ . Both samples were remelted further in order to obtain better homogeneity. Neutron diffraction patterns gave the same results. The phase corresponding to  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$  was also found in the samples after quenching from the melt.

In order to study the effect of heat treatment, the samples were sealed in evacuated quartz tube and annealed at different temperatures from 600 to 800°C for at least 50 hours and quenched in water. Neutron diffraction patterns showed extra peaks which could be indexed by the hexagonal unit cell corresponding to  $\text{Ni}_{1.3}\text{MnGe}_{0.7}$  with the original peaks corresponding to  $\text{Ni}_2\text{MnGe}$  and  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$  still be apparent but lower in intensities.

The best samples were obtained by annealing just below the melting point of the samples which was found to be around 1000°C. The appropriate annealing temperature and time are 950°C for about 100 hours. Neutron diffraction pattern showed that  $\text{Ni}_{1.3}\text{MnGe}_{0.7}$  disappeared and the peaks belong to  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$  were lowest.

In order to study the effect of varying the atomic composition, samples with atomic ratio of Ni-Mn-Ge of 2:1.1:1 and 2:1:1.1, corresponding to  $\text{Ni}_2\text{Mn}_{1.1}\text{Ge}$  and  $\text{Ni}_2\text{MnGe}_{1.1}$ , were prepared. Method of preparation is the same as described in (1). Neutron diffraction

patterns of both samples gave the same results as those found in  $\text{Ni}_2\text{MnGe}$  except a slight changes in relative intensities.

From the above results, it can be concluded that a single phase with the atomic composition close to  $\text{Ni}_2\text{MnGe}$  does not exist. The best result which give rise to a phase that is almost belong to the Heusler structure with a small amount of an additional phase can be obtained by annealing at  $950^\circ\text{C}$  for about 100 hours and quenching in water.

The obtained ingot of  $\text{Ni}_2\text{MnGe}$  sample was found to be weakly magnetic at room temperature and strongly magnetic at liquid nitrogen temperature by a hand magnet. The attraction between the hand magnet and the sample ingot is weaker when the ingot is warm up from liquid nitrogen temperature to room temperature. This shows that the sample is either ferromagnetic or ferrimagnetic with transition temperature close to room temperature. In order to study the magnetic structure of the sample by neutron diffraction, the second method described in section (III. 2) have been employed. The method involves measurements of neutron diffraction above and below the magnetic transition temperature. Since no significant change of Bragg reflections was found between powder diffraction patterns at about  $100^\circ\text{C}$  and room temperature. Therefore, the room temperature and liquid nitrogen temperature neutron diffraction patterns were used for this investigation.



#### IV. 3 Neutron Diffraction Measurements

Details of the chemical and magnetic structures were deduced from neutron diffraction measurements made above and below the magnetic ordering temperature, at room temperature ( $\sim 303$  K) and liquid nitrogen temperature ( $77$  K) respectively. The room temperature diffraction pattern was used to determine the state of atomic ordering in a unit cell which formed a basis for a construction of a model magnetic unit cell. The liquid nitrogen temperature diffraction pattern was used to determine the magnitude and direction of magnetic moments associated with magnetic atoms and to confirm the proposed model magnetic structure.

Neutron diffraction pattern at room temperature of powder  $\text{Ni}_2\text{MnGe}$  was obtained from the conventional double axis neutron spectrometer located at the TRR-1 reactor, Office of Atomic Energy for Peace. The powder diffraction pattern shown in figure 3 was taken using a cylindrical aluminum foil container of 9.6 mm diameter fully bathed vertically in neutron beam of wavelength  $\lambda = 1.167 \text{ \AA}$ . The Miller's indices were indexed using a lattice constant of  $5.7917 \text{ \AA}$ .

Neutron diffraction pattern at liquid nitrogen temperature was obtained using a liquid nitrogen cryostat supplied by the Bhabha Atomic Research Centre, India. The powder sample was filled in a cylindrical copper container attached to the bottom of the liquid nitrogen vessel. The vacuum in the cryostat was kept at  $\sim 5 \times 10^{-5}$  torr

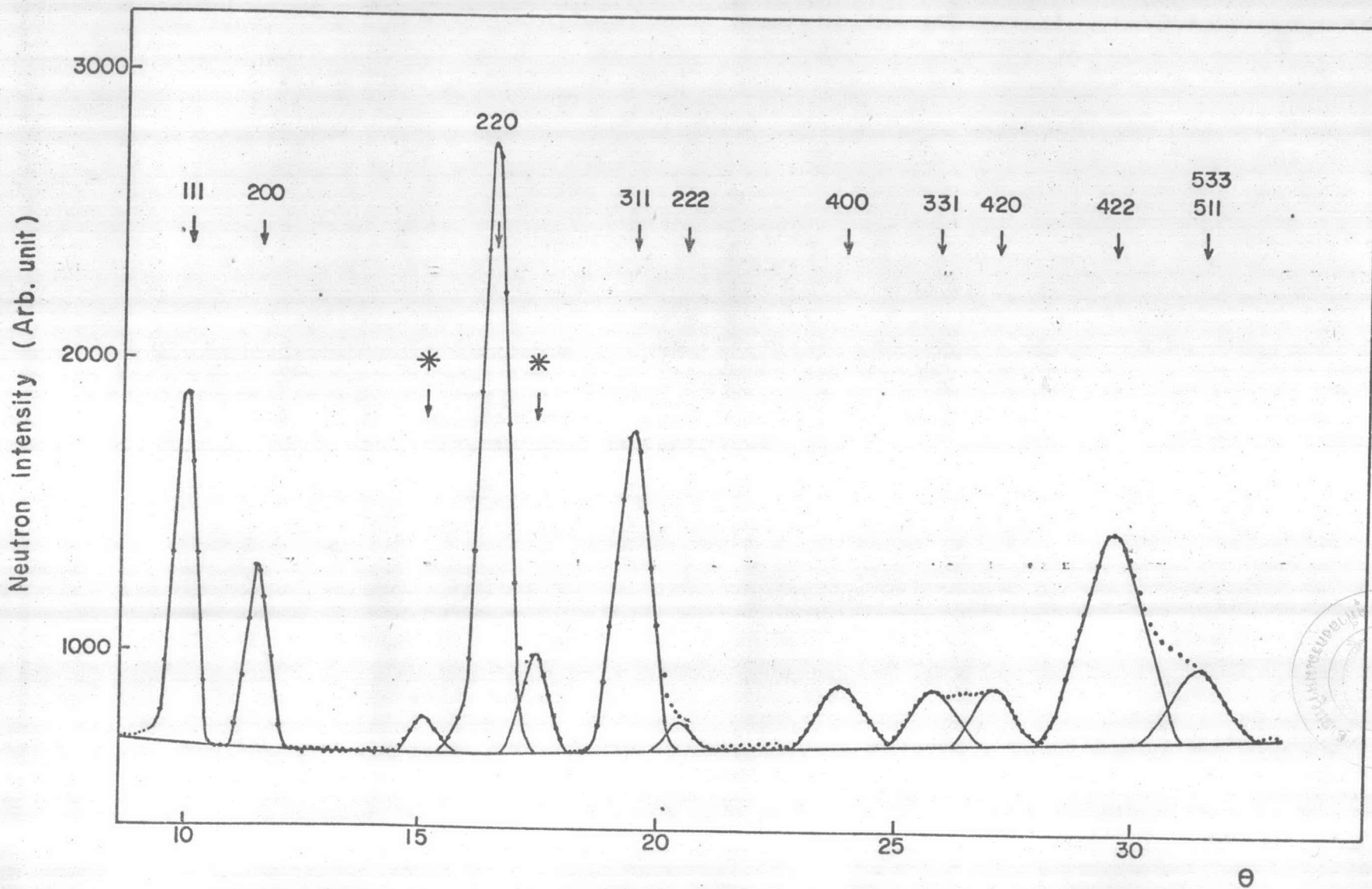


Fig. 3 Neutron diffraction pattern of  $\text{Ni}_2\text{MnGe}$  at room temperature. (\*  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$ )

by a diffusion-rotary pumps combinations. The temperature at the sample, measured by a copper-constantan thermocouple and a potentiometer, is 85 K. Since the magnetic form factor, as shown in figure 2 and table 4, decreases so rapidly that the magnetic scattering contribution at large angle are very small compared to the nuclear scattering. Therefore only the first three Bragg reflections were taken. This is shown in figure 4. In order to compare the neutron diffraction patterns at room and liquid nitrogen temperatures, the diffraction pattern at room temperature with the sample in the cryostat was also taken. This is also shown in figure 4.

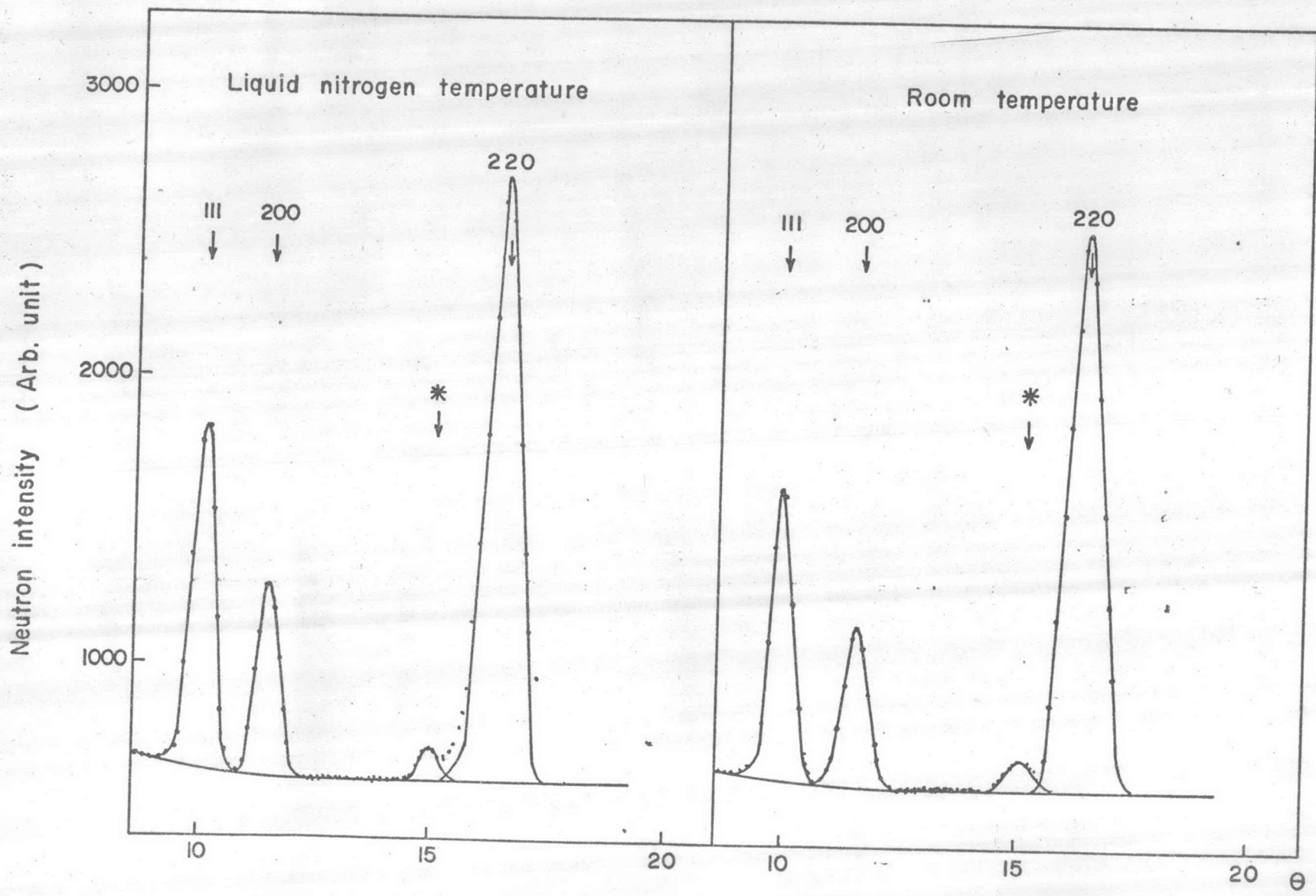
#### IV. 4 Chemical Order Determination

The analysis of the diffraction pattern at room temperature was done by the method discussed in chapter II and III. The intensities of Bragg reflections were first calculated using equation (8) and assuming a fully order  $L2_1$  structure. All factors involved in the calculation are shown in table 4. The principal reflection (220) was chosen as a normalization factor due to the fact that the structure factor is independent of chemical ordering of the unit cell. Results of the calculation were compared to the observed intensities. This is shown in table 5. It is clear that

hkl	$d \text{ (Å)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$	$\Theta = \text{arc. sin } \frac{\lambda}{2d}$	$\frac{L}{l} = \frac{1}{\sin \Theta \sin 2\Theta}$	j	f
111	3.3439	10° 2'	16.9866	8	.758
200	2.8958	11° 37'	12.5824	6	.688
220	2.0477	16° 34'	6.4233	12	.500
311	1.7463	19° 31'	4.7552	24	.390
222	1.6719	20° 25'	4.3831	8	.365
400	1.4479	23° 46'	3.3657	6	.260
331	1.3287	26° 2'	2.8887	24	.205
420	1.2951	26° 46'	2.7606	24	.190
422	1.1822	29° 34'	2.3610	24	-
511, 333	1.1146	31° 34'	2.1423	24,8	-

Table 4 Lattice spacing (d), Bragg angle ( $\Theta$ ), geometrical factor (L) multiplicity factor (j) and magnetic form factor (f) for  $\text{Ni}_2\text{MnGe}$ . ( $\lambda = 1.167 \text{ Å}$ ,  $a = 5.7917 \text{ Å}$ )





**Fig. 4** Neutron diffraction patterns of  $\text{Ni}_2\text{MnGe}$  at liquid nitrogen and room temperatures.  
 (\*  $\text{Ni}_{16}\text{Mn}_6\text{Ge}_7$ )

partial disorder of some types occurs. To determine the types and degree of disorder, the ratios  $jLF^2(111)/jLF^2(200)$  and  $jLF^2(200)/jLF^2(220)$ , with different degree of disorder ( $\alpha$ ) were calculated. The results are plotted and shown in figures 5 and 6. The dotted lines are the observed ratios. In simple case, where only one type of disorder present in the sample, the intersection of the experimental and the calculated value at the same value of  $\alpha$  for both ratios represent the state of disorder. But in this case it is not quite obvious. The intersections of the observed and calculated value are not at the same value of  $\alpha$ . It is likely that there are both random and preferential disorder present. The curves may then be used qualitatively to indicate the most likely type of preferential disorder, in this case type (4) and (5), and to eliminate other types. The degree of disorder may then be obtained by multiplying the experimental values by a factor  $1/S^2$ , where  $S$  is a measure of the degree of random disorder, until the experimental and calculated values intersect at one value of  $\alpha$ . In this experiment, this occurs at  $S^2 = .9174$ , with  $\alpha(5) = .575$ . The type (5) disorder is chosen on the reason that sublattices A and C are of the same element, and of almost the same surrounding. Therefore, there is no reason to regard that disorder might occur preferentially on sublattice A or C. From the value  $S^2 = .9174$ , the value  $\alpha(7) = .033$  is obtained. The sites scattering amplitudes were then calculated using expression given in table 2. The calculated and observed relative

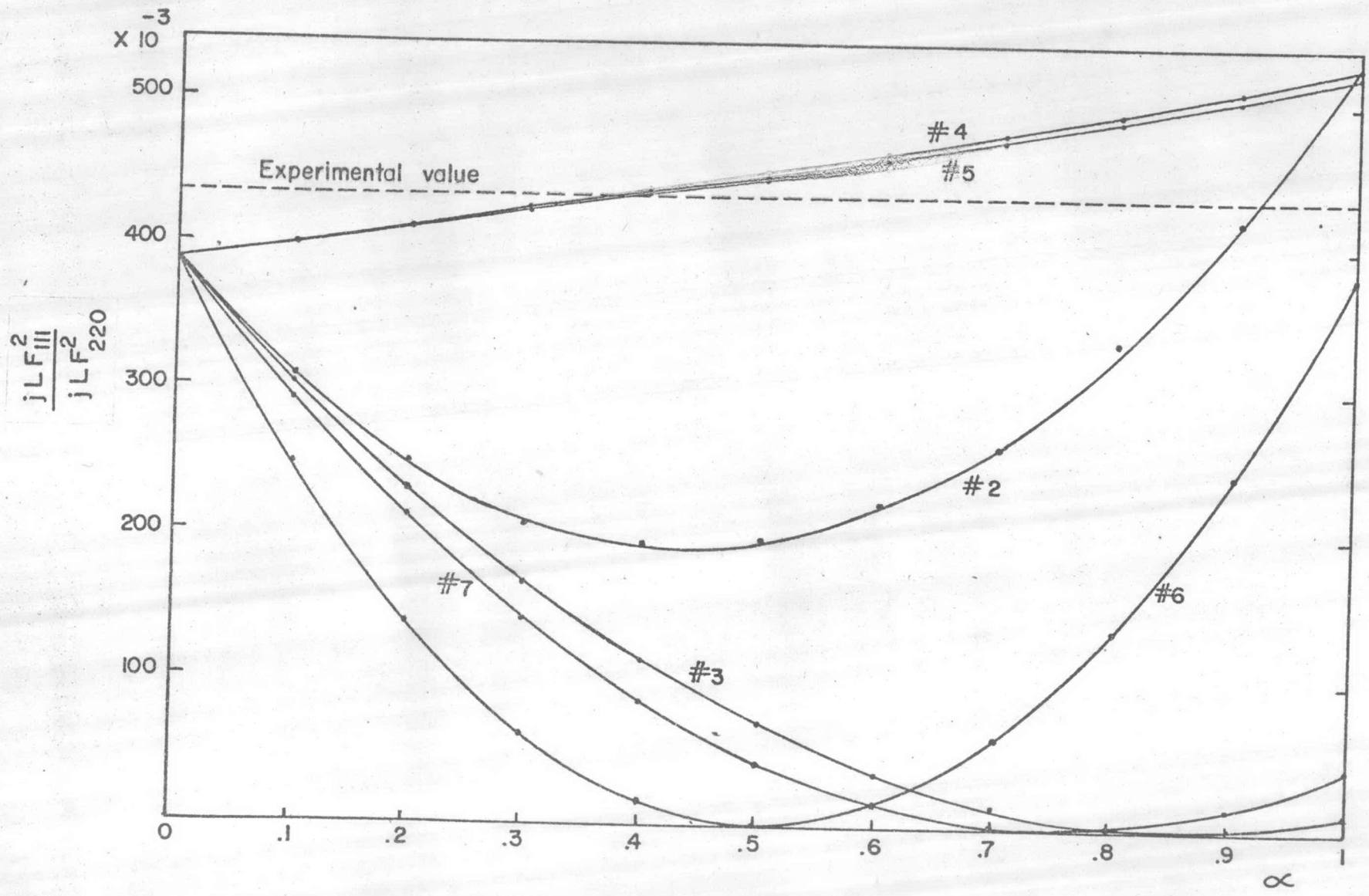


Fig. 5 Relative neutron diffraction intensity versus degree of disorder.

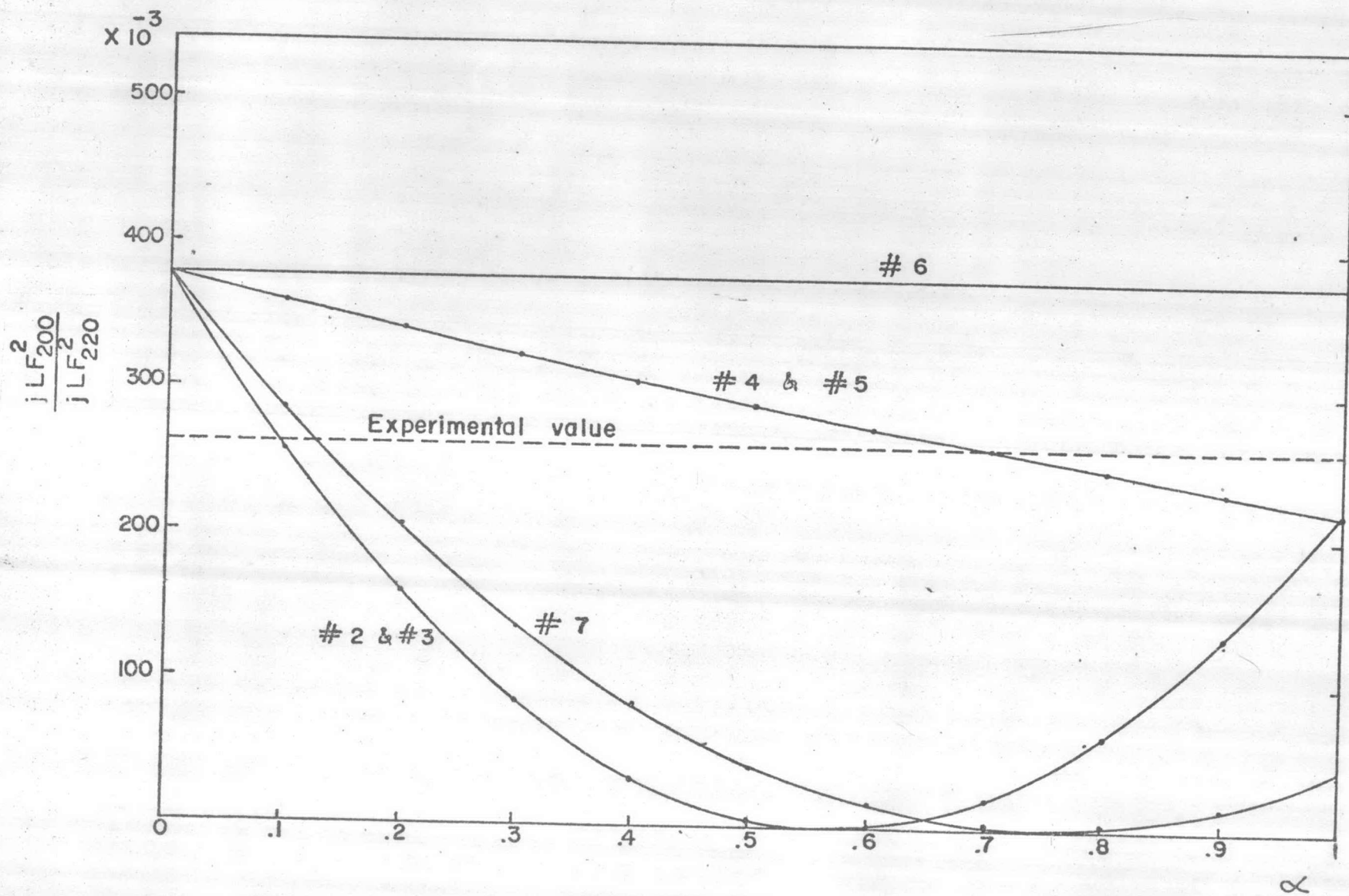


Fig. 6 Relative neutron diffraction intensity versus degree of disorder.



intensities with small adjustment by a temperature factor corresponding to  $B = .2 \times 10^{-16} \text{ cm}^2$  is shown in table 5.

#### IV. 5 Magnetic Structure Determination

It was discussed in section (2.3) that in most Heusler alloys containing manganese, the magnetic moment is confined to the manganese ion, and is usually about 4 Bohr magneton per atom. The series of Heusler alloys containing manganese and nickel  $\text{Ni}_2\text{MnGa}$ ,  $\text{Ni}_2\text{MnIn}$ ,  $\text{Ni}_2\text{MnSn}$  and  $\text{Ni}_2\text{MnSb}$ , as indicated in table 1, are no exception. The magnetic moment are about 4 Bohr magneton except for  $\text{Ni}_2\text{MnSb}$  which is 3.27 Bohr magneton.

In the present investigation, a magnetic unit cell, based on the results obtained from the chemical unit cell, was assumed. It was first assumed that manganese ions carry magnetic moment of 4 Bohr magneton per atom, and coupled ferromagnetically. Structure factors for Bragg reflections corresponding to planes (111), (200) and (220) were calculated employing equations (15), (16) and (17). Relative intensities were compared to observed intensities obtained at liquid nitrogen temperature. This is shown in table 6. The result is not in good agreement. The magnitude of magnetic moment was then adjusted in order to obtain a best fit between calculated and observed intensities. The best result was obtained when a 3.2 Bohr magneton was assumed. This is also shown in table 6.

hkl	Observed intensities	Calculated intensities			
		Fully ordered		$\alpha(5) = .575, \alpha(7) = .033$	
		$jLF^2$	%	$jLF^2 e^{-2w}$	%
111	43.50	3106	39.95	3379	43.46
200	26.27	2979	38.32	2021	26.01
220	100.00	7772	100.00	7772	100.00
311	} 52.27	2541	32.68	2763	35.56
222		1350	17.36	916	11.79
			} 50.04		} 48.35
400	23.85	1985	25.54	1985	25.54
331	22.42	1511	19.44	1644	21.14
420	21.74	2495	32.09	1692	21.78
422	80.92	5446	70.06	5446	70.06
511, 300	18.53	1456	18.73	1583	20.37

Table 5 Observed and calculated relative intensities of  $Ni_2MnGe$  at room temperature

hkl	Observed intensities	Calculated intensities				
		$jLFn^2$	$\mu_B = 4.0$		$\mu_B = 3.2$	
			$\frac{2}{3}jLF_m^2$	%	$\frac{2}{3}jLF_m^2$	%
111	49.87	3406	964	53.34	617	49.62
200	28.53	2046	441	30.36	282	28.72
220	100.00	7955	238	100.00	152	100.00

Table 6 Observed and calculate relative intensities of  $Ni_2MnGe$  at liquid nitrogen temperature