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Structure Determination of ζ_2-Mn_5Ge_2 Using a Mixed Crystal

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Abstract

$M_r = 419{\cdot}87$, trigonal, $P3c1$, $a = 7{\cdot}198\,(1)$, $c = 13{\cdot}076\,(1)$ Å, $V = 586{\cdot}7$ Å^3, $Z = 6$ (30 Mn and 12 Ge per unit cell), $D_x = 7{\cdot}129$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 31{\cdot}0$ mm^{-1}, $F(000) = 1134{\cdot}0$, $T = 295$ K. The crystal structure of ζ_2-Mn_5Ge_2 has been determined using diffraction data derived from a mixed crystal of ζ_1-$Mn_{5\cdot11}Ge_2$ and ζ_2-Mn_5Ge_2 whose c axis is one-third that of ζ_1, since it is difficult to isolate a pure single crystal of ζ_2. The analysis is performed on the assumption that the scattering from both crystallites is incoherent. The assumption has been proved to be valid by plotting the diffraction data obtained from a mixed crystal against those from pure ζ_1. Full-matrix least-squares refinement has been applied for 384 independent reflections derived from the mixed crystal, which leads to a final $R(F) = 0{\cdot}0885$, $wR(F) = 0{\cdot}0840$. The composition of ζ_2-Mn_5Ge_2 is found to be slightly different from ζ_1 by the structure analysis. The atoms in ζ_2-Mn_5Ge_2 are located in averaged positions for three parts of the ζ_1 structure which are obtained by dividing the structure into three along the c axis.

Introduction

There are five intermetallic compounds in the Mn–Ge system, *i.e.* $Mn_{3\cdot25}Ge$, Mn_5Ge_2, Mn_2Ge, Mn_5Ge_3 and $Mn_{11}Ge_8$. The crystal structures of these compounds have been determined and discussed by many authors, for example, Zwicker, Jahn & Schubert (1949), Kàdàr & Krèn (1971), Ohba, Ueyama, Kitano & Komura (1984), Ellner (1980), Castelliz (1953), Israiloff, Völlenkle & Wittmann (1974) and Ohba, Watanabe & Komura (1984). Of these, the structure of the high-temperature phase ζ-Mn_5Ge_2, which shows interesting magnetic behavior (Ohoyama, 1961; Wachtel & Henig, 1969; Yamada, Ohashi & Ohoyama, 1982; Yamada, Sakai, Usami & Ohoyama, 1986), is unknown.

An electron microscopic study of the high-temperature phase ζ-Mn_5Ge_2 was made by Kifune & Komura (1986) who found that two types of structures coexist in the alloy specimens and form microsyntactic intergrowth. These two structures have different c values, one is about 39 Å and the other 13 Å. We call the former ζ_1 and the latter ζ_2 in this paper. A mixed crystal of ζ_1 and ζ_2 shows double peaks in the temperature dependence of magnetization. The crystal structure of ζ_1-$Mn_{5\cdot11}Ge_2$ was determined using a specimen which showed no such double peaks but a single peak in the magnetization (Komura, Ohba, Kifune, Hirayama, Tagai, Yamada & Ohoyama, 1987).

Intensities of ζ_2-Mn_5Ge_2 have been separated from a mixed crystal of ζ_1 and ζ_2 with the method described in this paper. Intensity data thus derived have been used to determine the crystal structure of ζ_2-Mn_5Ge_2, since it is found to be difficult to isolate a pure single crystal of ζ_2.

Experimental

Intensity measurements have been made for three different crystal fragments. One is a single crystal ζ_1 of irregular shape, maximum dimension 0·09 mm (sample A), and the other two are mixtures of ζ_1 and ζ_2, maximum dimensions 0·06 and 0·12 mm (samples B and B'). All the intensity data were collected on a Rigaku automated four-circle diffractometer (AFC-5), with graphite-monochromated Mo $K\alpha$ radiation. An ω scan was employed because of the long c axis of the ζ_1 crystal. Experimental conditions for sample A have already been reported (Komura *et al.*, 1987). Conditions for sample B: lattice constants estimated from interplanar spacings are $a = 7{\cdot}198\,(1)$, $c = 13{\cdot}076\,(1)$ and $3c = 39{\cdot}227\,(4)$ Å (mixture) using 25 reflections ($19° < 2\theta < 41°$), scan range $(1{\cdot}5 + 0{\cdot}5\tan\theta)°$, scan rate 2° min^{-1} in θ, background measurements at the beginning and the end of each scan range for 5 s and the ranges of the data collected were $-9 \le h \le 9$, $-9 \le k \le 9$, $0 \le l \le 50$ and $2° \le 2\theta \le 50°$; 1337 measured reflections with $|F_o| \ge 3\sigma(|F_o|)$ averaged to 768 independent reflections. Experimental conditions for sample B' are almost the same as those for B. Lp and absorption corrections were applied for the samples A and B, but not for B'.

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Analysis of the mixed structure

A. Comparison of the two kinds of data sets

We have three data sets. One was obtained from a ζ_1 single crystal having a simple magnetization curve (Komura *et al.*, 1987) and the other two were obtained from the mixed crystals of ζ_1 and ζ_2. The data collected from the ζ_1 single crystal are called data A and the others from mixed crystals data B and B'. The data sets B and B' did not give good reliability factors when the structure refinements of ζ_1 were made (Komura & Hirayama, 1981). The final R factors obtained were about 10%, and they were not reduced any more. Some atoms have negative temperature factors and some others anomalously large values. As described before, the structure of ζ_1-$Mn_{5\cdot 11}Ge_2$ has been analyzed satisfactorily by using data A (Komura *et al.*, 1987). The structure of the second phase ζ_2 has been solved with data B or B'.

The intensities from samples A and B are represented respectively as follows:

$$I^A(\mathbf{h}) = k^A I_{39}(\mathbf{h}) \qquad (1A)$$

and

$$I^B(\mathbf{h}) = k^B[n_{39}I_{39}(\mathbf{h}) + (1-n_{39})I_{13}(\mathbf{h})], \qquad (1B)$$

where $\mathbf{h}$ is a reciprocal-lattice vector, k^A and k^B are scale factors for samples A and B, respectively, $I_{13}(\mathbf{h})$ is the intensity from ζ_2, $I_{39}(\mathbf{h})$ is that from ζ_1, and $n_{39}(0 \le n_{39} \le 1)$ is the fraction of ζ_1 in sample B. We assume here that X-rays are scattered incoherently by ζ_1 and ζ_2 in the mixed crystal and that structure factors can be calculated by the kinematical diffraction theory. The c axis of ζ_1 is exactly three times that of ζ_2. The intensity of an hkl reflection having $l = 3n$ in the mixed crystal is considered to be the sum of the intensities from ζ_1 and ζ_2. On the other hand, $I_{13}(\mathbf{h})$ is equal to zero for reflections with $l \neq 3n$ [(1B)]. Here the index l is referred to the longer c axis (ζ_1). The following relations between $I^A(\mathbf{h})$ and $I^B(\mathbf{h})$ can be obtained from (1A) and (1B) for $l \neq 3n$ and $l = 3n$:

$$I^A(\mathbf{h}) = (k^A/k^B n_{39}) I^B(\mathbf{h}) \qquad \text{for } l \neq 3n \qquad (2)$$

$$I^A(\mathbf{h}) = (k^A/k^B n_{39}) I^B(\mathbf{h}) - (k^A/n_{39})(1-n_{39}) I_{13}(\mathbf{h}) \qquad \text{for } l = 3n. \qquad (3)$$

Equations (2) and (3) show that $I^A(\mathbf{h})$ is proportional to $I^B(\mathbf{h})$ for $l \neq 3n$ reflections, but it is not for $l = 3n$ reflections. $I^A(\mathbf{h})$ for $l = 3n$ reflections are smaller than $I^B(\mathbf{h})$ multiplied by the scale-factor ratio $k^A/k^B n_{39}$.

Fig. 1 shows the correlation of intensities between two data sets A and B, where the intensities are plotted as $\log|F|$. The symbols $\times$ and $\bigcirc$ in Fig. 1 represent intensities for $l = 3n$ and $l \neq 3n$ reflections, respectively. It is clearly shown that $l = 3n$ reflections are distributed lower than $l \neq 3n$ reflections. Another data set B' was also compared with data A, and a similar distribution was obtained. Weaker reflections, which are distributed in the lower left part of the figure, are scattered.

B. Derivation of the ζ_2-Mn_5Ge_2 structure

(i) *Intensity of the ζ_2-Mn_5Ge_2 structure.* Intensity $I_{13}(\mathbf{h})$ for $l = 3n$ can be obtained from (3) by subtracting the intensity $I^A(\mathbf{h})$ from the intensity $I^B(\mathbf{h})$ multiplied by $k^A/k^B n_{39}$. Although n_{39}, k^A and k^B are not known, $k^A/k^B n_{39}$ can be determined by a comparison of reflections with $l \neq 3n$ [(2)].

A ratio (p) of the structure factor of data A to that of B, $p = |F_A(\mathbf{h})|/|F_B(\mathbf{h})|$, which is related to $k^A/k^B n_{39}$ in (2) and (3), is calculated for every reflection. Averaged values of p are calculated for $l = 3n$ ($\bar{p}_{l=3n}$) and $l \neq 3n$ ($\bar{p}_{l\neq 3n}$) and are $\bar{p}_{l=3n} = 2{\cdot}985\,(5)$ and $\bar{p}_{l\neq 3n} = 5{\cdot}000\,(3)$ for 411 and 297 reflections, respectively. It is reasonable for $\bar{p}_{l=3n}$ to be smaller than $\bar{p}_{l\neq 3n}$ because the intensity of reflection with $l = 3n$ for B comes from both crystals of ζ_1 and ζ_2 [(2) and (3)]. The value $k^A/k^B n_{39}$ should be equal to $\bar{p}^2_{l\neq 3n}$ according to (2). The intensity $I_{13}(\mathbf{h})$ is proportional to $\bar{p}^2_{l\neq 3n}|F_B(\mathbf{h})|^2 - |F_A(\mathbf{h})|^2$ according to (3).

For mixed crystals, we have two data sets, B and B'. If the data for $I_{13}(\mathbf{h})$ derived from both B and B' are compared, one can expect a linear relation between them. 199 $I'_{13}(\mathbf{h})/I_{13}(\mathbf{h})$ are plotted in Fig. 2, where $I_{13}(\mathbf{h})$ and $I'_{13}(\mathbf{h})$ are the intensities derived from B and B', respectively. A linear relationship can be observed. Three strong reflections, 030, 300 and 1,1,15, however, deviate from the linear relationship, but these reflections in data set B' are affected strongly by extinction owing to the large size of crystal B'.

The structure of ζ_2 can be analyzed using $I_{13}(\mathbf{h})$ derived from the mixed crystal as described above.

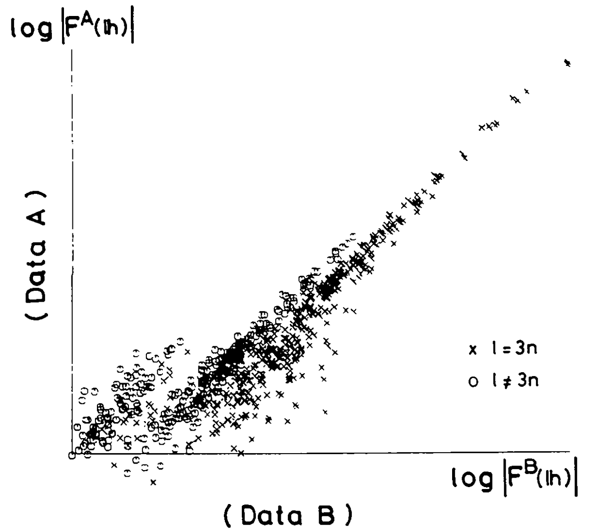

Fig. 1. Comparison of two data sets A and B. Marks $\times$ and $\bigcirc$ represent $l = 3n$ and $l \neq 3n$ reflections, respectively.

(ii) *Model of the* ζ_2-Mn_5Ge_2 *structure.* The intensity distribution of $I_{13}(\mathbf{h})$ for the ζ_2 structure derived from the mixed crystal is very similar to that for ζ_1 with $l=3n$. Intensity distributions of reciprocal nets $0kl$ for ζ_1 and ζ_2 are shown schematically in Figs. 3(*a*) and (*b*), respectively. Patterson maps synthesized from $I_{13}(\mathbf{h})$ are also similar to those of ζ_1, so that it may be reasonable to assume that the two crystal structures resemble each other. To obtain an initial model of ζ_2-Mn_5Ge_2, the structure of ζ_1 (Komura *et al.*, 1987) is divided into three parts along the *c* axis (Fig. 4*a*) and the atoms are assumed to be located on the average positions for the three parts (Fig. 4*b*). There are two kinds of fundamental layers stacked alternately at $c/30$ in ζ_1. Additional atoms are placed on three threefold axes. Atomic positions in the three parts are very similar except for atoms on $00z$, so that average positions of the atoms on $\frac{1}{3}\frac{2}{3}z$, $\frac{2}{3}\frac{1}{3}z$ and fundamental layers are easily obtained. Atomic positions on $00z$ of the three parts of ζ_1 are superposed and schematically drawn on a line as shown in Fig. 5. Mn atoms for the initial model of ζ_2 were placed between two v marks and Ge atoms were placed between two + marks. Refinements of the ζ_2 structure have been carried out using the full-matrix least-squares method described below.

C. Refinement of the ζ_2-Mn_5Ge_2 *structure*

The scale factor and positional parameters were refined firstly using 384 independent $I_{13}(\mathbf{h})$ reflections derived from data set *B*, and the *R* value reached 0·0945 with a fixed temperature factor of $B_o = 0{\cdot}8$ Å^2. After refinement with temperature factors, the final *R* value was $R(F)=0{\cdot}0885$, $wR(F)=0{\cdot}0840$, $w=1$, $s=1{\cdot}0937$, $(\Delta/\sigma)_{max}=0{\cdot}07$ and $\Delta\rho$ excursions $\le|11|$ e Å^{-3}.* The temperature factors have reasonable values. Determination of the polar direction has not been attempted. The final atomic parameters are listed in Table 1. The program used in the refinement was *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) and scattering factors and anomalous-dispersion corrections f' and f'' for Mn and Ge atoms were taken from *International Tables for X-ray Crystallography* (1974).

* A list of structure factors for ζ_2-Mn_5Ge_2 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44108 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

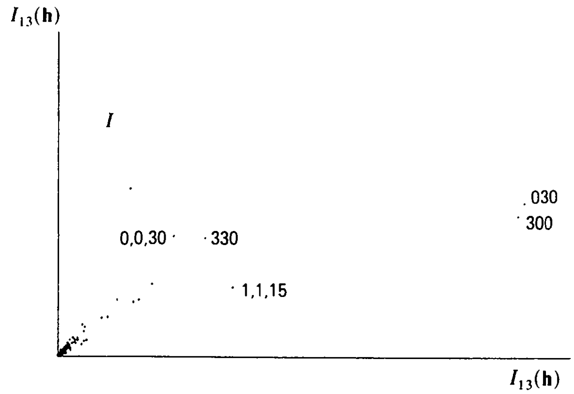

Fig. 2. Comparison of $I_{13}(\mathbf{h})$ and $I'_{13}(\mathbf{h})$ derived from data sets *B* and *B'*, respectively.

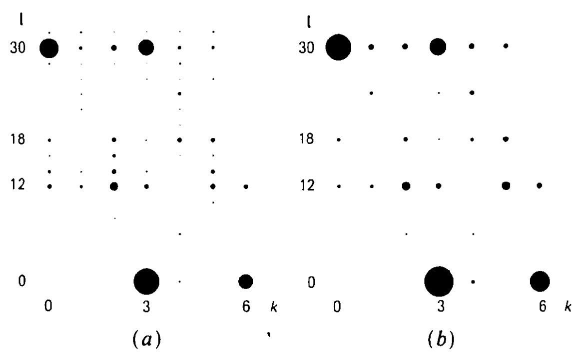

Fig. 3. Intensity distributions of the reciprocal nets $0kl$ for (*a*) ζ_1 and (*b*) ζ_2 structures. Index *l* is referred to the ζ_1 structure.

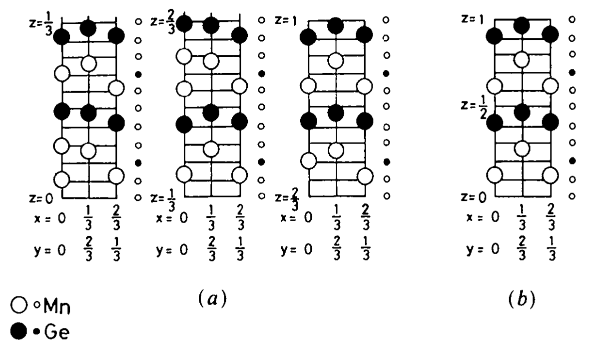

Fig. 4. Initial model projected along [010]. Fundamental layers and three threefold axes are represented by horizontal and vertical lines, respectively. Mn and Ge atoms on the threefold axes are represented by open and filled circles, respectively. Kinds of atoms in the fundamental layers are shown by small open and filled circles beside the horizontal lines. (*a*) ζ_1 structure divided into three parts and (*b*) initial model of ζ_2 structure.

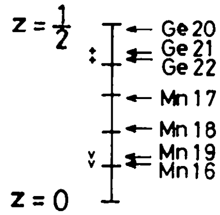

Fig. 5. Superposed atomic positions on the 00z axis of the three parts of ζ_1-$Mn_{5\cdot11}Ge_2$. The *z* parameter is referred to ζ_2-Mn_5Ge_2.

Table 1. *Atomic parameters for* ζ_2-Mn_5Ge_2

B_o is an isotropic temperature factor. Designation of atoms is followed in the ζ_1 structure.

		x	y	z	B_o(Å^2)
Mn(1)	6(d)	0·3339 (17)	0·0295 (15)	0·0	0·78 (15)
Mn(4)	6(d)	0·6121 (13)	−0·0545 (13)	0·0945 (11)	0·75 (12)
Ge(7)	6(d)	0·3338 (10)	−0·0065 (13)	0·1951 (11)	1·11 (9)
Mn(10)	6(d)	0·6916 (20)	0·0257 (20)	0·2963 (11)	1·91 (21)
Mn(13)	6(d)	0·3312 (25)	−0·0239 (20)	0·3900 (6)	1·10 (17)
Mn(16)	2(a)	0·0	0·0	0·1201 (14)	0·97 (25)
Ge(21)	2(a)	0·0	0·0	0·4125 (12)	1·19 (17)
Ge(23)	2(b)	$\frac{1}{3}$	$\frac{2}{3}$	−0·0343 (14)	1·38 (18)
Mn(26)	2(b)	$\frac{1}{3}$	$\frac{2}{3}$	0·2681 (22)	1·62 (27)
Mn(29)	2(c)	$\frac{2}{3}$	$\frac{1}{3}$	0·1212 (15)	0·75 (25)
Ge(32)	2(c)	$\frac{2}{3}$	$\frac{1}{3}$	0·4138 (12)	1·06 (20)

NO	NV	$R(F)$	$wR(F)$	S
384	32	0·0885	0·0840	1·0937

Table 2. *Interatomic distances* (Å^2) *for* ζ_2-Mn_5Ge_2

Mn(1)–Ge(32)	2·560 (10)
Ge(7)	2·564 (14)
Ge(21)	2·573 (13)
Ge(23)	2·648 (13)
Mn(10)	2·664 (14)
Mn(4)	2·668 (17)
Mn(4)	2·672 (13)
Mn(13)	2·758 (24)
Mn(16)	2·789 (15)
Mn(29)	2·792 (13)
Mn(13)	2·827 (13)
Mn(13)	2·844 (25)
Mn(4)	2·862 (16)
Mn(4)–Ge(7)	2·560 (16)
Ge(7)	2·564 (16)
Ge(23)	2·620 (16)
Mn(16)	2·639 (10)
Mn(29)	2·641 (10)
Mn(1)	2·668 (17)
Mn(1)	2·672 (13)
Mn(13)	2·684 (16)
Mn(10)	2·700 (19)
Mn(1)	2·862 (16)
Mn(26)	3·029 (24)
Ge(7)	3·130 (12)
Ge(7)–Mn(26)	2·537 (15)
Mn(13)	2·552 (16)
Mn(1)	2·564 (14)
Mn(4)	2·560 (16)
Mn(4)	2·564 (16)
Mn(29)	2·607 (11)
Mn(16)	2·617 (12)
Mn(10)	2·624 (20)
Mn(10)	2·800 (18)
Mn(10)	2·812 (15)
Mn(4)	3·130 (12)
Mn(10)–Mn(26)	2·608 (11)
Ge(7)	2·624 (20)
Mn(1)	2·664 (14)
Mn(13)	2·679 (17)
Mn(4)	2·700 (19)
Mn(13)	2·711 (24)
Mn(13)	2·727 (23)
Ge(21)	2·772 (18)
Ge(32)	2·774 (18)
Ge(7)	2·800 (18)
Ge(7)	2·812 (15)
Mn(29)	3·251 (20)
Mn(16)	3·268 (20)
Mn(13)–Ge(23)	2·444 (18)
Ge(21)	2·492 (20)
Ge(32)	2·516 (12)
Ge(7)	2·552 (16)
Mn(10)	2·679 (17)
Mn(4)	2·684 (16)
Mn(10)	2·711 (24)
Mn(10)	2·727 (23)
Mn(26)	2·745 (22)
Mn(1)	2·758 (24)
Mn(1)	2·827 (13)
Mn(1)	2·844 (25)
Mn(16)–3Ge(7)	2·617 (12)
3Mn(14)	2·639 (10)
Ge(21)	2·715 (24)
3Mn(1)	2·789 (15)
3Mn(10)	3·268 (20)
Ge(21)–3Mn(13)	2·492 (20)
3Mn(1)	2·573 (13)
Mn(16)	2·715 (24)
3Mn(10)	2·772 (18)
Ge(23)–3Mn(13)	2·444 (18)
Mn(26)	2·584 (34)
3Mn(4)	2·620 (16)
3Mn(1)	2·648 (13)
Mn(26)–3Ge(7)	2·537 (15)
Ge(23)	2·584 (34)
3Mn(10)	2·608 (11)
3Mn(13)	2·745 (22)
3Mn(4)	3·029 (24)
Mn(29)–3Ge(7)	2·607 (11)
3Mn(4)	2·641 (10)
Ge(32)	2·712 (25)
3Mn(1)	2·792 (13)
3Mn(10)	3·251 (20)
Ge(32)–3Mn(13)	2·516 (12)
3Mn(1)	2·560 (10)
Mn(29)	2·712 (25)
3Mn(10)	2·774 (18)

The refinement was also made using intensities $I_{13}(\mathbf{h})$ derived from data set B'. The positional parameters obtained are the same as those of B within 3σ. Since we reach the same results for the structure from the different data sets, it is concluded that the structure of ζ_2-Mn_5Ge_2 is determined correctly.

Discussion

The structure of ζ_2-Mn_5Ge_2, whose c axis is one-third of ζ_1-$Mn_{5\cdot11}Ge_2$, has been determined using the intensities derived from a mixed crystal. As described above, we already know the structure of ζ_1-$Mn_{5\cdot11}Ge_2$ (Komura *et al.*, 1987). If the calculated intensity data $I_{39}(\mathbf{h})$ from the ζ_1 structure are substituted in (1B), with k^Bn_{39} known from (2) for $l \neq 3n$, the intensity data $I_{13}(\mathbf{h})$ can be obtained independently from the above method. The structure refinement has been carried out using this data set and the positional parameters thus obtained lead to the same values within errors of 3σ. We utilized one data set from a pure single crystal in this paper. However, this method can be applied even without having single-crystal data if one has two data sets of mixed crystals of different compositions.

The composition of ζ_2 is slightly different from ζ_1 according to the refinement; the number of Mn atoms on 00z is two for ζ_2 and eight for ζ_1 even though the c axis is three times longer than that of ζ_2 (Fig. 5). ζ_2 is then described exactly by Mn_5Ge_2, and ζ_1 by $Mn_{5\cdot11}Ge_2$. The difference between them is small, and it is practically impossible to distinguish them by chemical analysis since both crystallites make microsyntactic intergrowth.

Interatomic distances for ζ_2-Mn_5Ge_2 are listed in Table 2. The coordination number of Mn atoms in ζ_2 is 12 or 13 and that of Ge atoms 10 or 11, which is similar to the ζ_1 structure.

The crystallites of ζ_2 make microsyntactic intergrowth with ζ_1 as was observed under the electron microscope (Kifune & Komura, 1986). The width of the bands of intergrowth is about 1000 Å. Although an effort to find a single crystal of ζ_2-Mn_5Ge_2 was made, no such crystal was obtained even under the electron microscope. The validity of the treatment of the incoherent-scattering calculation from both crystallites is apparent in Fig. 1. If coherent scattering is dominant, cross terms of F and F^* appear in (1B). In general, cross terms of F and F^* cannot be known as positive or negative. So $l = 3n$ reflections are distributed randomly above and below $l \neq 3n$ reflections. Weaker reflections, which are distributed in the lower left part in Fig. 1, are seen to form two groups. Attempts to find the reason have not yet succeeded.

It is remarkable that the difference in the structure may reflect sensitively on the magnetic properties. It is necessary to obtain a single domain of ζ_2 in order to find the detailed relationship between the structure and the magnetic properties.

The calculations were carried out on a HITAC M-200H computer at the Information Processing Center of Hiroshima University and a personal computer, Fujitsu FM-11EX, in our laboratory.

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