Acta Cryst. (1984). **B40**, 351–354

Temperature Dependence of the Lattice Constants and the Structure of $Mn_{11}Ge_8$ at 295 and 116 K

By T. Ohba, N. Watanabe* and Y. Komura

Department of Materials Science, Faculty of Science, Hiroshima University, Higashi-senda-machi, Naka-ku, Hiroshima 730, *Japan*

(*Received* 23 *December* 1983; *accepted* 13 *February* 1984)

Abstract

$M_r = 1185{\cdot}04$, orthorhombic, *Pnam*, $a = 13{\cdot}214\,(2)$, $b = 15{\cdot}880\,(3)$, $c = 5{\cdot}0905\,(5)$ Å, $V = 1068{\cdot}2$ Å^3, $Z = 4$, $\mu(\text{Mo }K\alpha) = 35{\cdot}54\ \text{mm}^{-1}$, $D_x = 7{\cdot}37\ \text{Mg m}^{-3}$, $\lambda = 0{\cdot}71069$ Å, $R(F) = 0{\cdot}0326$ at 295 K. The crystal structure of $Mn_{11}Ge_8$, formerly considered to be Mn_3Ge_2, has been refined using a single crystal at 295 and 116 K. The temperature dependence of the lattice constants shows that a kink appears at the temperature (160 K) where the magnetic transition from a weak ferromagnetic to an antiferromagnetic state takes place. Although the crystal symmetry does not change, the positional parameters above and below the transition temperature show non-uniform changes of interatomic distances. The Mn–Mn interatomic distances change more than Mn–Ge or Ge–Ge, and some Mn–Mn distances are even expanded at 116 K. The deformation densities along the Mn–Mn bond vary considerably from 295 to 116 K.

Introduction

Zwicker, Jahn & Schubert (1949) reported four intermetallic compounds in the Mn–Ge system: $Mn_{3{\cdot}25}Ge$, Mn_5Ge_2, Mn_5Ge_3 and Mn_3Ge_2. $Mn_{3{\cdot}25}Ge$ has high- and low-temperature phases whose structure types are Ni_3Sn ($D0_{19}$) (Zwicker *et al.*, 1949) and Al_3Ti ($D0_{22}$) (Kádár & Krén, 1971), respectively. Mn_5Ge_2 also has high- and low-temperature phases. The high-temperature ζ phase was found by Ohoyama (1961) and the structure was first reported by Komura & Hirayama (1981). The low-temperature κ phase has been found by Ohba, Ueyama, Kitano & Komura (1984) to be orthorhombic (*Ibam*) by the single-crystal X-ray diffraction method. The η phase, Mn_5Ge_3, has the Mn_5Si_3 ($D8_8$) type structure (Castelliz, 1953). In addition, the χ phase Mn_2Ge was found during the study of magnetic properties (Wachtel & Henig, 1969), and has the Ni_2In ($B8_2$) type structure (Ellner, 1980). Zavadskii & Fakidov (1967) reported that Mn_3Ge_2 is an antiferromagnet at low temperature and transforms to a weak ferromagnet at 160 K. The transition was thought to be first-order (Flippen & Darnell, 1963). Israiloff, Völlenkle & Wittmann (1974) reported that Mn_3Ge_2 is isotypic with $Cr_{11}Ge_8$ by a comparison of powder diffraction patterns. In this paper, the crystal structure of $Mn_{11}Ge_8$ is examined by the single-crystal X-ray diffraction method at 116 and 295 K; the temperature dependence of the lattice constants is also measured using a single crystal.

Experimental

Mn_5Ge_3 mother alloys prepared by melting 99·99% Mn flakes and 99·999% Ge in an alumina crucible placed in an evacuated quartz tube at 1420 K. $Mn_{11}Ge_8$ alloy ingot was melted after addition of the necessary amount of Ge at 1420 K and was annealed at 970 K for 50 h. For the structure analysis, single crystals were selected from tiny fragments of crushed ingot. The shape of the crystal examined was a cylinder 36 μm in diameter and 180 μm in length. The specimen was recognized as a single crystal from Laue and oscillation photographs: orthorhombic, *Pnam*, systematic absences $0kl$ with $k+l \neq 2n$ and $h0l$ with $h \neq 2n$. Lattice constants determined by least-squares method using 25 relatively strong reflections ($44° < 2\theta < 68°$), Rigaku automated four-circle diffractometer (AFC-5), Mo $K\alpha_1$ radiation ($\lambda = 0{\cdot}70926$ Å), temperature range 295 to 116 K at intervals of 20 K, temperature controlled by blowing a stream of nitrogen gas directly on the crystal; space group *Pnam* does not change even at the temperature of magnetic transition (160 K); lattice constants at 295 (2) K are $a = 13{\cdot}214\,(2)$, $b = 15{\cdot}880\,(3)$, $c = 5{\cdot}0905\,(5)$ Å, and at 116 (0·2) K are $a = 13{\cdot}173\,(2)$, $b = 15{\cdot}817\,(3)$, $c = 5{\cdot}0671\,(4)$ Å. Integrated intensities at both temperatures collected on the same diffractometer (AFC-5), graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan, reflections collected in a quarter of reciprocal space out to $2\theta = 70°$, scan range $(1{\cdot}3 + 0{\cdot}5\tan\theta)°$, scan rate 2° min^{-1} in θ, backgrounds measured at the beginning and end of each scan range for 5 s, Lp corrections at each scan; reflections not satisfying the condition $\sigma(|F_o|)/|F_o| < 0{\cdot}1$ measured twice; weak reflections ($|F_o| < 3{\cdot}0$) remeasured more precisely if $\sigma(|F_o|)/|F_o| < 0{\cdot}01$.

---

* Present address: Manufacturing Development Laboratory, Mitsubishi Electric Corporation, Amagasaki, Japan.

0108-7681/84/040351-04$01.50

Refinement

The structure was refined at 295 and 116 K with, respectively, 1898 and 1964 independent reflections obtained by averaging symmetry-related reflections with $|F_o| > 3\sigma(|F_o|)$. Absorption correction [μ(Mo $K\alpha$) = 35·54 mm^{-1}] applied, crystal assumed to approximate a sphere of radius 25 μm. Refinements with the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979); $w = 1/\sigma^2(|F_o|)$. Positional parameters of $Cr_{11}Ge_8$ adopted as starting values of the least-squares refinement. Parameters refined: a scale factor, positional parameters, isotropic temperature factors, and an isotropic extinction parameter. Scattering factors and anomalous-dispersion corrections f' and f'' for Mn and Ge atoms from *International Tables for X-ray Crystallography* (1974). $R_w(F)$ 0·0446 and 0·0324 at 295 and 116 K, respectively. Anisotropic temperature factors then introduced; $R_w(F)$ 0·0292 and 0·0260 at 295 and 116 K, respectively.* $(\Delta/\sigma)_{max}$ 0·30 and 0·33 at 295 and 116 K, respectively. $\Delta\rho$ excursions $\le |2{\cdot}4|$ e Å^{-3} at 295 K and $\le |1{\cdot}5|$ e Å^{-3} at 116 K. Calculations carried out with HITAC M-180 and M-200H computers at the Information Processing Center of Hiroshima University.

Results, discussion and relation between interatomic distances and magnetic properties

The temperature dependence of the lattice constants is drawn in Fig. 1, which shows a kink at the transition temperature of about 160 K. Flippen & Darnell (1963) reported the magnetic transition of this material to be first order. However, the figure does not show any gap at the transition temperature.

Refined parameters at 295 and 116 K are shown in Table 1. The shifts of the positional parameters from those of $Cr_{11}Ge_8$ are greater than the standard deviations. The **c** projection of the structure at 295 K is shown in Fig. 2. The structure is constructed by four layers stacked along the c axis. The layers at $z \simeq 0$ and $\frac{1}{2}$ consist of triangles and squares, connected with solid lines in Fig. 2. There are five triangles and a square around Ge atoms in these layers. The triangles have Mn and Ge atoms above and below the planes ($z = \frac{1}{4}$ and $\frac{3}{4}$); then two tetrahedra are formed, sharing each triangle at $z \simeq \frac{1}{2}$. Mn atoms on $z = \frac{1}{4}$ and $\frac{3}{4}$ in the tetrahedra are placed rather close to the Ge atom on the layer $z \simeq \frac{1}{2}$. There are four Mn atoms and two Ge atoms above and below the square. These four Mn atoms are also close to the Ge atom placed at the

Table 1. *Refined parameters for* $Mn_{11}Ge_8$

$U_{eq} = \frac{1}{3}$ trace **U**.

(a) At 295 K

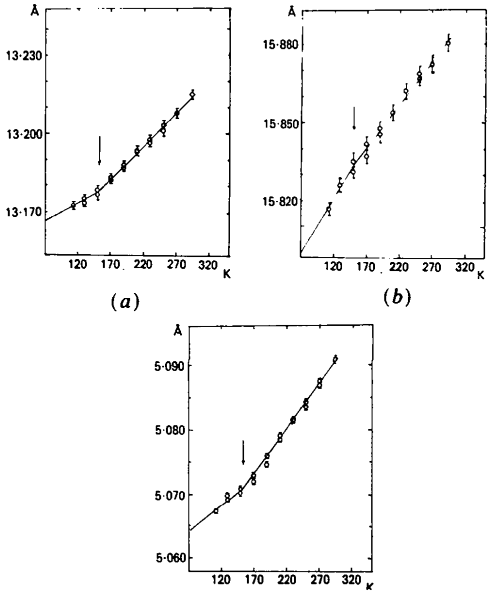
	Site	x	y	z	U_{eq}(Å^2)
Mn(1)	8(d)	0·36465 (6)	0·32437 (5)	−0·00686 (17)	0·0091 (3)
Mn(2)	8(d)	0·06067 (6)	0·37890 (5)	−0·00049 (18)	0·0095 (3)
Mn(3)	4(c)	0·06768 (9)	0·19394 (9)	$\frac{1}{4}$	0·0119 (5)
Mn(4)	4(c)	0·36844 (9)	0·04234 (8)	$\frac{1}{4}$	0·0123 (5)
Mn(5)	4(c)	0·13419 (9)	0·65746 (7)	$\frac{1}{4}$	0·0100 (5)
Mn(6)	4(c)	0·24900 (9)	0·46945 (8)	$\frac{1}{4}$	0·0130 (5)
Mn(7)	4(c)	0·45324 (9)	0·59370 (8)	$\frac{1}{4}$	0·0134 (6)
Mn(8)	4(c)	0·12338 (9)	0·99428 (8)	$\frac{1}{4}$	0·0139 (5)
Mn(9)	4(c)	0·30674 (9)	0·74885 (8)	$\frac{1}{4}$	0·0099 (5)
Ge(1)	8(d)	0·21470 (4)	0·11435 (3)	0·00368 (13)	0·0100 (2)
Ge(2)	4(c)	0·20439 (6)	0·30379 (5)	$\frac{1}{4}$	0·0100 (4)
Ge(3)	4(c)	0·41639 (6)	0·19580 (5)	$\frac{1}{4}$	0·0098 (3)
Ge(4)	4(c)	0·05509 (6)	0·51640 (5)	$\frac{1}{4}$	0·0099 (3)
Ge(5)	4(c)	0·45001 (6)	0·43718 (5)	$\frac{1}{4}$	0·0122 (4)
Ge(6)	4(c)	0·27490 (6)	0·90348 (5)	$\frac{1}{4}$	0·0095 (3)
Ge(7)	4(c)	0·49150 (6)	0·74509 (5)	$\frac{1}{4}$	0·0096 (3)

NO	NV	$R(F)$	$R_w(F)$	S	g
1898	107	0·0326	0·0292	1·1862	0·46 (1) × 10^{-4}

(b) At 116 K

	Site	x	y	z	U_{eq}(Å^2)
Mn(1)	8(d)	0·36329 (5)	0·32484 (4)	−0·00653 (15)	0·0049 (3)
Mn(2)	8(d)	0·05970 (5)	0·37888 (4)	−0·00054 (15)	0·0050 (3)
Mn(3)	4(c)	0·06735 (8)	0·19317 (6)	$\frac{1}{4}$	0·0062 (4)
Mn(4)	4(c)	0·36910 (7)	0·04272 (6)	$\frac{1}{4}$	0·0062 (4)
Mn(5)	4(c)	0·13480 (7)	0·65786 (6)	$\frac{1}{4}$	0·0052 (4)
Mn(6)	4(c)	0·24924 (8)	0·46961 (6)	$\frac{1}{4}$	0·0065 (4)
Mn(7)	4(c)	0·45248 (7)	0·59364 (6)	$\frac{1}{4}$	0·0063 (4)
Mn(8)	4(c)	0·12340 (8)	0·99388 (6)	$\frac{1}{4}$	0·0065 (4)
Mn(9)	4(c)	0·30755 (7)	0·74882 (6)	$\frac{1}{4}$	0·0051 (4)
Ge(1)	8(d)	0·21454 (3)	0·11397 (3)	0·00366 (11)	0·0051 (2)
Ge(2)	4(c)	0·20312 (5)	0·30428 (4)	$\frac{1}{4}$	0·0052 (3)
Ge(3)	4(c)	0·41594 (5)	0·19659 (4)	$\frac{1}{4}$	0·0050 (3)
Ge(4)	4(c)	0·05587 (5)	0·51642 (4)	$\frac{1}{4}$	0·0051 (3)
Ge(5)	4(c)	0·44964 (5)	0·43744 (4)	$\frac{1}{4}$	0·0061 (3)
Ge(6)	4(c)	0·27586 (5)	0·90390 (4)	$\frac{1}{4}$	0·0050 (3)
Ge(7)	4(c)	0·49268 (5)	0·74448 (4)	$\frac{1}{4}$	0·0049 (3)

NO	NV	$R(F)$	$R_w(F)$	S	g
1964	107	0·0299	0·0260	1·0647	0·36 (1) × 10^{-4}



(a) (b)

(c)

Fig. 1. Temperature dependence of the lattice constants: (a) a axis; (b) b axis; (c) c axis. Arrows indicate kinks on the curves.

---

* Lists of structure factors and anisotropic temperature factors for $Mn_{11}Ge_8$ at 295 and 116 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39268 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *for* $Mn_{11}Ge_8$

	295 K	116 K
Mn(1)–Mn(1)	2·4754 (13)	2·4674 (11)
	2·6151 (13)	2·5997 (11)
Mn(3)	2·9987 (14)	2·9994 (12)
Mn(5)	2·9253 (14)	2·9152 (12)
Mn(6)	3·0583 (14)	3·0315 (12)
Mn(7)	3·0026 (14)	3·0123 (11)
Mn(8)	2·9727 (15)	2·9498 (12)
Mn(9)	2·8459 (14)	2·8342 (11)
Ge(2)	2·5102 (11)	2·4994 (9)
Ge(3)	2·5191 (11)	2·5071 (9)
Ge(5)	2·4882 (11)	2·4810 (9)
Ge(6)	2·5516 (11)	2·5388 (9)
Ge(7)	2·5223 (11)	2·5147 (9)
Mn(2)–Mn(2)	2·5403 (13)	2·5281 (11)
	2·5502 (13)	2·5390 (11)
Mn(3)	3·2032 (16)	3·2016 (12)
Mn(4)	3·0376 (15)	3·0320 (12)
	3·1052 (14)	3·0746 (11)
Mn(5)	2·9286 (14)	2·9155 (11)
Mn(6)	3·1443 (14)	3·1473 (12)
Mn(9)	2·9913 (14)	2·9812 (11)
Ge(2)	2·5798 (11)	2·5638 (9)
Ge(3)	2·5822 (11)	2·5735 (9)
Ge(4)	2·5296 (11)	2·5193 (9)
	2·5918 (11)	2·5803 (9)
Ge(6)	2·5469 (11)	2·5390 (9)
Ge(7)	2·5698 (11)	2·5677 (9)
Mn(3)–Mn ×4		
Mn(7) ×2	3·0148 (11)	2·9942 (8)
Mn(8)	3·2551 (20)	3·2375 (15)
Mn(9) ×2	3·1610 (11)	3·1479 (9)
Ge(1) ×2	2·6352 (13)	2·6243 (10)
Ge(2)	2·5111 (16)	2·5074 (12)
Ge(3)	2·6574 (16)	2·6492 (12)
Ge(5)	2·5988 (16)	2·5830 (12)
Ge(7) ×2	2·7838 (7)	2·7754 (5)
Mn(4)–Mn ×4		
Mn(5) ×2	3·1339 (10)	3·1206 (8)
Mn(6) ×2	3·1979 (11)	3·1916 (9)
Mn(8)	3·3269 (18)	3·3275 (15)
Ge(1) ×2	2·6471 (12)	2·6407 (10)
Ge(3)	2·5180 (16)	2·5108 (12)
Ge(4)	2·6369 (15)	2·6322 (12)
×2	2·7693 (6)	2·7512 (5)
Ge(6)	2·5279 (15)	2·5159 (12)
Mn(5)–Mn ×6		
Mn(6)	3·3489 (18)	3·3374 (15)
Mn(9)	2·7028 (17)	2·6923 (14)
Ge(1) ×2	2·4745 (12)	2·4643 (9)
Ge(3) ×2	2·7011 (5)	2·6909 (4)
Ge(4)	2·4719 (14)	2·4670 (12)
Ge(7)	2·4392 (14)	2·4271 (12)
Mn(6)–Mn ×7		
Mn(7)	3·3432 (18)	3·3191 (14)
Mn(8) ×2	3·0786 (10)	3·0628 (9)
Ge(1) ×2	2·6819 (13)	2·6633 (10)
Ge(2)	2·6959 (16)	2·6847 (12)
Ge(4)	2·6686 (15)	2·6527 (13)
Ge(5)	2·7051 (15)	2·6885 (13)
Ge(6) ×2	2·7705 (6)	2·7583 (5)
Mn(7)–Mn ×5		
Mn(8)	2·6470 (17)	2·6430 (14)
×2	3·1616 (11)	3·1477 (8)
Mn(9)	3·1333 (18)	3·1096 (14)
Ge(1) ×2	2·5884 (12)	2·5683 (10)
Ge(5)	2·4859 (16)	2·4709 (12)
×2	2·8902 (7)	2·8850 (6)
Ge(7)	2·4567 (16)	2·4439 (12)
Mn(8)–Mn ×9		
Ge(1) ×2	2·5815 (13)	2·5705 (10)
Ge(5)	2·5363 (15)	2·5336 (13)
×2	2·8707 (7)	2·8533 (6)
Ge(6)	2·4674 (15)	2·4615 (12)
Mn(9)–Mn ×8		
Ge(1) ×2	2·5119 (13)	2·5072 (10)
Ge(2) ×2	2·6946 (6)	2·6848 (4)
Ge(6)	2·4913 (16)	2·4882 (12)
Ge(7)	2·4422 (15)	2·4397 (12)

Table 2 (*cont.*)

	295 K	116 K
Ge(1)–Mn ×7		
Ge(1)	2·5827 (10)	2·5706 (8)
	2·5078 (10)	2·4965 (8)
Ge(2)	3·2620 (10)	3·2622 (9)
Ge(3)	3·2169 (10)	3·2101 (8)
Ge(2)–Mn ×8		
Ge ×2		
Ge(3)	3·2846 (12)	3·2804 (10)
Ge(6) ×2	3·0099 (7)	2·9964 (5)
Ge(3)–Mn ×8		
Ge ×3		
Ge(7) ×2	2·9734 (6)	2·9558 (5)
Ge(4)–Mn ×9		
Ge(4) ×2	2·9781 (6)	2·9758 (5)
Ge(5)–Mn ×10		
Ge(6)–Mn ×9		
Ge ×2		
Ge(7)–Mn ×9		
Ge ×2		

corner of the square. If we compare the positional parameters at 295 K with those at 116 K, it is recognized that the shifts of the parameter x of Mn(2), Mn(7), Mn(9) and Ge(4) are more than ten times larger than the shifts of parameters y or z of those atoms, and the shift of parameter y of Mn(8) is larger than that of parameter x. The average shifts of the parameters x for all atoms are larger than those of y and z. Interatomic distances calculated from these parameters are shown in Table 2. They show that the distances are not contracted uniformly at low temperature; for example, the distances Mn(1)–Mn(3), Mn(1)–Mn(7), Mn(2)–Mn(6) and Mn(4)–Mn(8) are expanded. In particular, the change of the distances Mn(1)–Mn(7) is five times larger than the standard deviation [$\Delta d = 0{\cdot}0097\ (18)$ Å]. All the Ge–Ge and Mn–Ge interatomic distances are contracted at low temperature. The histogram of the changes of the interatomic distances ($\Delta d = d_{295} - d_{116}$) is shown in

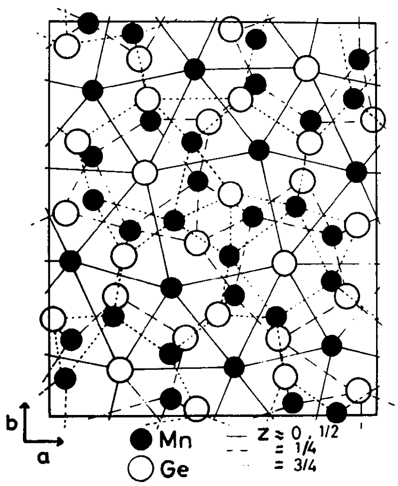


Fig. 2. The **c** projection of the $Mn_{11}Ge_8$ structure at 295 K.

Fig. 3. The changes of Mn–Mn distance are more widely scattered than those of Mn–Ge and Ge–Ge. The average changes ($\overline{\Delta d} = \sum|\Delta d|/n$) of Mn–Mn, Mn–Ge and Ge–Ge are 0·0145, 0·0105 and 0·0091 Å, respectively. The magnetic properties of Mn alloys in the Mn–Pt system are thought to be strongly affected by the Mn–Mn distances (Krén, Kádár, Pal, Solyom, Szabó & Tarnóczi, 1968). The above distribution of interatomic distances suggests that the contribution of Mn–Mn distances to magnetic properties in $Mn_{11}Ge_8$ is considerable.

The thermal vibrations in real space are calculated using the thermal parameters. Mn(7), Mn(8) and Ge(5) show characteristic vibrations. The thermal ellipsoids of these atoms are elongated in the [001] direction compared to the other principal axes; this is because these atoms have relatively large space along the [001] direction. The principal axes of thermal motion of the atoms are approximately along the *a*, *b* and *c* axes. The ratios of the thermal motion along the principal axes at the two temperatures are different for different axis directions; that is, the ratio along the *a* axis is larger than along the other axes. This suggests that the elastic constants at low temperature are different from those at room temperature.

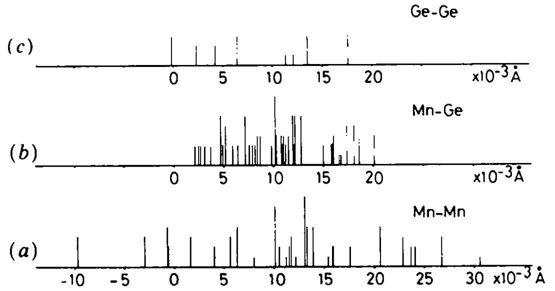


Fig. 3. The histogram of the changes of the interatomic distances ($\Delta d = d_{295} - d_{116}$): (*a*) Mn–Mn; (*b*) Mn–Ge; (*c*) Ge–Ge.

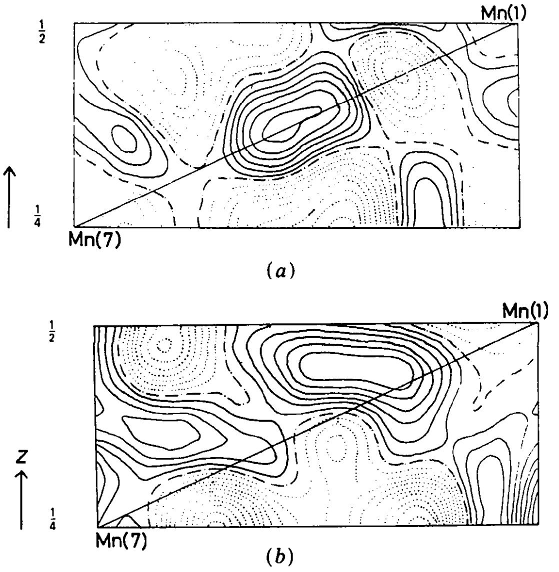


Fig. 4. The deformation densities on the plane which contains the Mn(1)–Mn(7) bond and the *c* axis (*a*) at 295 and (*b*) 116 K. The contour interval is 0·1 e Å^{-3} and solid and dotted lines represent positive and negative contours, respectively.

The coordination numbers of the Mn atoms are between 13 and 17 and those of the Ge atoms are between 10 and 13. The Mn(1) and Mn(2) atoms placed on $z \simeq 0$ and $\frac{1}{2}$ have fewer nearest neighbors than the other Mn atoms on $z = \frac{1}{4}$ and $\frac{3}{4}$. Only Ge(5) is surrounded entirely by 10 unlike atoms.

Differences in the electron density distribution of $Mn_{11}Ge_8$ at the two temperatures may be expected owing to the change of magnetic property; for example at the middle of the Mn(1)–Mn(7) bond, whose interatomic distance is expanded at low temperature. Fig. 4 shows the deformation density on the plane which contains the Mn(1)–Mn(7) bond and the *c* axis. At 295 K the highest positive peak along Mn(1)–Mn(7) is found near the center of Mn(1)–Mn(7) and the highest negative peak about 0·75 Å from Mn(1), while at 116 K the negative peak disappears and the positive region, which spreads parallel to **c**, is found about 0·85 Å from Mn(1). The difference may be reflected in the magnetic properties of $Mn_{11}Ge_8$.

The authors thank Mr Kifune of Hiroshima University for his cooperation in this work. The present work has partly been supported by a Scientific Research Grant from the Ministry of Education, Science and culture, to which the authors' thanks are due.

References

Castelliz, L. (1953). *Monatsh. Chem.* **84**, 765–776.

Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. D. & Yang, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.

Ellner, M. (1980). *J. Appl. Cryst.* **13**, 99–100.

Flippen, R. B. & Darnell, F. J. (1963). *J. Appl. Phys.* **34**, 1094–1095.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Israiloff, P., Völlenkle, H. & Wittmann, A. (1974). *Monatsh. Chem.* **105**, 1387–1404.

Kádár, G. & Krén, E. (1971). *Int. J. Magn.* **1**, 143–148.

Komura, Y. & Hirayama, H. (1981). *Acta Cryst.* **A37**, C-184–C-185.

Krén, E., Kádár, G., Pal, L., Solyom, J., Szabó, P. & Tarnóczi, T. (1968). *Phys. Rev.* **171**, 574–585.

Ohba, T., Ueyama, K., Kitano, Y. & Komura, Y. (1984). *Acta Cryst.* **C40**, 576–579.

Ohoyama, T. (1961). *J. Phys. Soc. Jpn*, **16**, 1995–2002.

Wachtel, E. & Henig, E.-T. (1969). *Z. Metallkd.* **60**, 243–247.

Zavadskii, E. A. & Fakidov, I. G. (1967). *Sov. Phys. JETP*, **24**, 887–889.

Zwicker, U., Jahn, E. & Schubert, K. (1949). *Z. Metallkd.* **40**, 433–436.