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The Crystal Structure of MnAs above 40 °C

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The crystal structure of MnAs between 40 and 125 °C has been found to be of the MnP (B_{31}) type, with $a=5{\cdot}72$, $b=3{\cdot}676$ and $c=6{\cdot}379$ Å, space group *Pnma* (D_{2h}^{16}). The orthorhombic cell is very close in dimensions to the orthohexagonal cell of a hexagonal structure and twinning invariably occurs to give pseudo-hexagonal symmetry. The atomic parameters have been deduced from intensity data for twinned crystals obtained at 55 °C with a precession camera. The distortions from a NiAs type structure are like those in MnP but less in magnitude. The extent of the distortion was found to be temperature dependent and to disappear at 125 °C with a reversion to a NiAs type structure, which occurs also below 40 °C.

Introduction

Manganese arsenide (MnAs) at room temperature has the NiAs ($B8_1$) structure and is ferromagnetic. At 40 °C*, however, there occurs a first order phase transition as indicated by changes in volume, specific heat, resistivity and magnetization (Bean & Rodbell, 1962). In particular, the ferromagnetism disappears abruptly. A further transition takes place at 125 °C*, but this appears to be of the second order type.

Previous crystallographic studies (Willis & Rooksby, 1954), limited to polycrystalline specimens, have indicated a preservation of the NiAs type structure over all temperatures but with a large discontinuity in lattice parameter at 40 °C — specifically, a 1% decrease in *a* with rising temperature (the *c* axes remaining essentially unchanged). Our preliminary observations with X-rays on polycrystalline samples seemed in accord with these findings, but a neutron diffraction powder pattern at 55 °C revealed discrepancies with the expected pattern, especially in the occurrence of some small peaks not indexable for a NiAs type cell. While, at first, the possibility that the strange peaks were of magnetic origin could not be ruled out, it seemed more likely that a change of crystal structure occurred above 40 °C. Single-crystal studies appeared in order, then, and these demonstrated quite clearly, as will be detailed, that between 40 °C and 125 °C MnAs is not of the NiAs structure type but in fact has an orthorhombic structure of the MnP type, although the distortions from a hexagonal NiAs structure are small and difficult to detect with X-ray powder techniques. The work reported here is mainly that concerning single-crystal *X-ray* diffraction results in the range 40 °C to 125 °C.

Experimental

A variety of appropriately small crystals were studied, mainly by the precession technique with Mo $K\alpha$ radiation, but some supplementary data were obtained with counter methods. These crystals were selected from an abundant supply kindly provided by D. S. Rodbell of this laboratory. They occurred in an ingot prepared from stoichiometric proportions of the elements which were vacuum melted and then cooled slowly in a temperature gradient. While many crystals were examined and it was verified that the diffraction effects were the same for all of them, the intensity data of Table 1 used for structural analysis are those of an individual crystal with dimensions $0{\cdot}06\times0{\cdot}15\times0{\cdot}45$ mm. No chemical analysis of the crystals was made; they were assumed to contain the stoichiometric proportions of the elements.

A temperature of 55 °C ± 5 °C was used for the study of the structure beyond the first transition. This temperature was achieved simply by focusing the light from the filaments of two small lamp bulbs onto the crystal. For the observations beyond the second transition the temperature was maintained at 130 °C ± 5 °C by means of a stream of hot air directed at the crystal. The temperatures were measured by a thermocouple placed close to the crystal.

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* The MnAs phase exists over a range of compositions and the exact transition temperatures are dependent on composition.

Table 1. *Observed and calculated* F^2_{hkl}

(*a*) Single reflections, $k+l=2n+1$

hkl	$F_o^2/10$	$F_c^2/10$	*hkl*	$F_o^2/10$	$F_c^2/10$	*hkl*	$F_o^2/10$	$F_c^2/10$
101	—	0·02	503	39	30	127	32	26
201	15	11	423	79	77	532	121	100
210	112	111	225	—	6	434	18	16
112	101	129	116	73	81	614	6	13
103	82	106	332	16	9	136	25	40
212	10	11	216	28	27	227	—	2
301	168	197	521	69	68	623	114	117
203	88	81	134	12	15	712	34	44
121	—	0·2	405	42	34	236	16	14
221	7	7	601	17	21	118	61	67
312	19	15	430	61	63	525	148	144
303	*	53	610	172	195	343	13	10
114	37	44	234	—	3	407	14	10
401	69	71	325	—	1	441	11	17
123	51	55	107	45	38	605	13	18
410	116	128	316	44	50	703	13	8
214	2	6	514	9	14	516	48	39
321	118	121	141	—	0·2	218	—	4
223	56	52	432	39	29	630	67	104
105	148	169	612	15	21	327	114	112
412	55	62	523	24	20	721	92	90
403	117	110	603	169	160	336	22	26
205	—	8	207	—	3	534	8	8
314	196	250	241	—	3	145	37	38
230	44	44	334	115	117	632	12	12
501	87	96	505	239	197	443	37	30
323	33	31	425	26	24	318	—	4
132	53	43	621	15	15	245	—	2
421	45	47	143	18	15	507	—	1
232	9	5	307	201	151	714	101	135
305	—	2	341	38	40	541	20	27
125	114	107	416	37	51	801	40	37
414	34	32	701	96	122			
512	178	199	243	19	18			

* Present, but no reliable measurement made.

(*b*) Composite reflections, $k+l=2n$

hkl	$\Sigma F_o^2/100$	$F_c^2/100$
000	—	538
002	—	5
(2) 101	—	15
	16	20
200	5	4
102	—	78
(2) 111	—	158
	174	236
202	—	123
(2) 211	—	246
	>250	369
020	—	224
(2) 013	—	401
	>250	625
113	—	0
302	—	37
(2) 311	—	84
	118	121

hkl	$\Sigma F_o^2/100$	$F_c^2/100$
004	—	1
(2) 022	—	2
	2	3
220	—	5
(2) 213	—	16
	16	21
104	—	47
(2) 122	—	90
	112	137
400	86	124
204	—	49
(2) 222	—	136
	159	185
313	—	0
402	—	2
(2) 411	—	5
	10	7
304	—	30
(2) 322	—	50
	71	80

hkl	$\Sigma F_o^2/100$	$F_c^2/100$
015	—	1
024	—	0
031	—	1
	—	2
115	—	29
124	—	31
131	—	31
	83	91
420	—	78
(2) 413	—	140
	232	218
215	—	32
224	—	31
231	—	42
	113	105
502	—	14
(2) 511	—	26
	37	40
404	—	0
(2) 422	—	2
	—	2

Table 1 (*cont.*)

hkl	$\Sigma F_o^2/100$	$F_c^2/100$
006	—	58
(2) 033	—	158
	193	216
106	—	0
(2) 133	—	0
	—	0
315	—	15
324	—	21
331	—	19
	49	55
206	—	12
(2) 233	—	10
	19	22
513	—	2
600	—	1
504	—	8
(2) 522	—	20
	30	28
306	—	1
(2) 333	—	0
	—	1
415	—	8
424	—	17
431	—	79
	91	104
040	—	60
(2) 026	—	81
	131	141
602	—	17
(2) 611	—	36
	54	53
126	—	2
017	—	1
035	—	1
042	—	0
	—	2
240	—	3
(2) 226	—	17
	17	20
117	—	16
135	—	14
142	—	15
	34	45
406	—	24
(2) 433	—	66
	96	90
217	—	7
235	—	15
242	—	21
	38	43
620	—	0
(2) 613	—	0
	—	0
515	—	8
524	—	6
531	—	6
	21	20
326	—	0
604	—	9
(2) 622	—	24
	42	33
317	—	12
335	—	8
342	—	8
	24	28
008	—	3
(2) 044	—	0
	—	3
108	—	10
(2) 144	—	23
	48	33
702	—	2
(2) 711	—	6
	10	8
506	—	0
(2) 533	—	0
	—	0
440	—	27
(2) 426	—	35
	78	62
208	—	6
(2) 244	—	22
	51	28
417	—	0
435	—	0
442	—	0
	—	0
615	—	6
624	—	6
631	—	10
	31	22
713	—	1
308	—	5
(2) 344	—	16
	37	21
028	—	2
037	—	1
051	—	0
	—	3
128	—	8
137	—	9
151	—	7
	43	24
704	—	3
(2) 722	—	3
	7	6
526	—	4
517	—	3
535	—	4
542	—	4
	13	11
019	—	10
046	—	16
053	—	22
	62	48
119	—	0
146	—	0
153	—	0
	—	0
715	—	1
724	—	2
731	—	2
	6	5
617	—	2
635	—	4
642	—	5
	18	11

Most of the intensity data were obtained with the precession camera. The measurements were made visually by comparison with a standard scale of intensities. Lorentz-polarization corrections were computed with an IBM 704 program. A relatively few measurements were also made with a proportional counter and the General Electric single-crystal orienter, in order to fill out the sphere of reflection (for Mo $K\alpha$) or to provide better measurements when the photographic data were deficient. No absorption corrections were applied.

Structure determination

The twinning phenomenon

It was immediately evident from the precession photographs that above 40 °C the structure of MnAs was different from the NiAs type because of the occurrence of extra reflections. The diffraction effects were somewhat subtle, however, and the structure solution could only proceed following the recognition that twinning was present. There are two classes of reflections: (1) A strong set indexable for a NiAs cell with an a of 3·68 Å and c of 5·72 Å, with hexagonal symmetry in the intensity distribution. With these reflections alone there would be agreement with Willis & Rooksby (1954) that a 1% shrinkage in a occurs (a=3·72 Å at room temperature) with essentially no change in c; (2) a weaker set, seemingly indexable for a hexagonal cell with an a twice that mentioned above but without hexagonal symmetry in the intensity distribution. Considerations of intensity distribution made it appear very improbable that the diffraction effects were due to a single crystal of whatever symmetry, but they could be readily interpreted for a twinned orthorhombic structure whose unit cell is dimensionally close to the orthohexagonal cell of the implied NiAs cell.

Fig. 1 gives schematically the reciprocal lattice and shows the relationship between the NiAs type cell and the three orthorhombic twins (not in equivalent proportions). It is to be noted that the orthorhombic cell is primitive and that there is no overlap in the new, weaker reflections from the different twins. The three different intensities at successive 60° intervals at a given radial distance therefore give a measure of the proportions of the twins. Observations on different crystals gave different intensity ratios for reflections so related, in support of the twinning hypothesis.

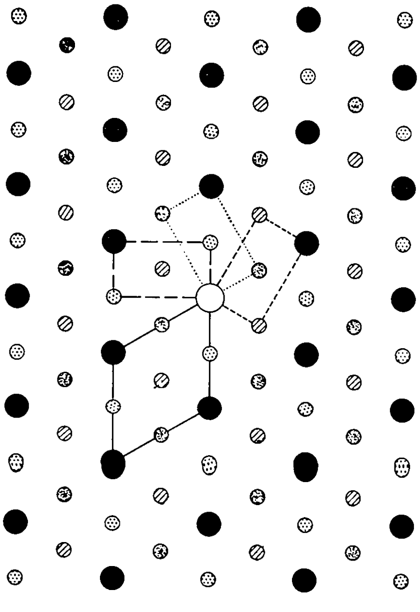

Fig. 1. Reciprocal lattice for MnAs above 40 °C projected normal to the pseudo-sixfold axis. The large black circles indicate the lattice for a NiAs type structure and also represent the overlapping of reflections from the 3 orthorhombic twins. The 3 twins correspond to the 3 orientations of the orthohexagonal cell. They are distinguished by the different shadings of the small circles.

It follows, also, that the stronger reflections at positions corresponding to a NiAs cell would be superpositions of reflections from all the twins and hence would tend to exhibit hexagonal symmetry, as observed photographically. The fact that from the precession photographs no deviation dimensionally from a hexagonal lattice could be detected and no distinction could be made in the character of the two kinds of reflections means that the orthorhombic cell is indeed very close to an orthohexagonal one whose axial ratio is $\sqrt{3}$. This was verified by observations at large Bragg angles with a proportional counter and a single-crystal orienter. Thus, the reflections with $k+l=2n+1$ were found to be single, while a superposition of reflections occurred at the other kinds of positions. Fig. 2 illustrates the latter situation for what would be {220} reflections of the pseudohexagonal cell but properly are combinations of 400 and 026 orthorhombic reflections. The differences in Figs. 2(a), 2(b), 2(c) are to be expected from the differences in the proportions of the twins, in this case approximately 4:2:1. From the counter measurements the orthorhombic cell dimensions were deduced as a= 5·72 Å, b=3·676 Å, c=6·379 Å (Fig. 3). The ratio c/b is 1·735 compared to 1·732 for an orthohexagonal cell. Kornelsen (1961) has observed a splitting of large angle reflections in studies of polycrystalline material from which he deduces an orthorhombic cell of a=5·724, b=3·66$_8$, c=6·36$_7$ at 51 °C in sufficiently good agreement with our results.

During the transition at 40 °C and the concomitant twinning there is exact preservation of the orientation of the c axis of the low temperature hexagonal phase as the common axis of the three twins. Even more remarkable is the circumstance that the proportions of different twins are always the same for repeated cyclings through the transition. Both these situations made it readily possible to obtain the desired diffraction data at 55 °C over extended periods of time once a single crystal was properly oriented at room temperature.

Space group and structural parameters

Accepting the orthorhombic nature of the unit cell, the systematic absences were those characteristic of space group *Pnma*. We have chosen a crystal setting to conform to the description in the space group tables of the *International Tables for X-ray Crystallo-*

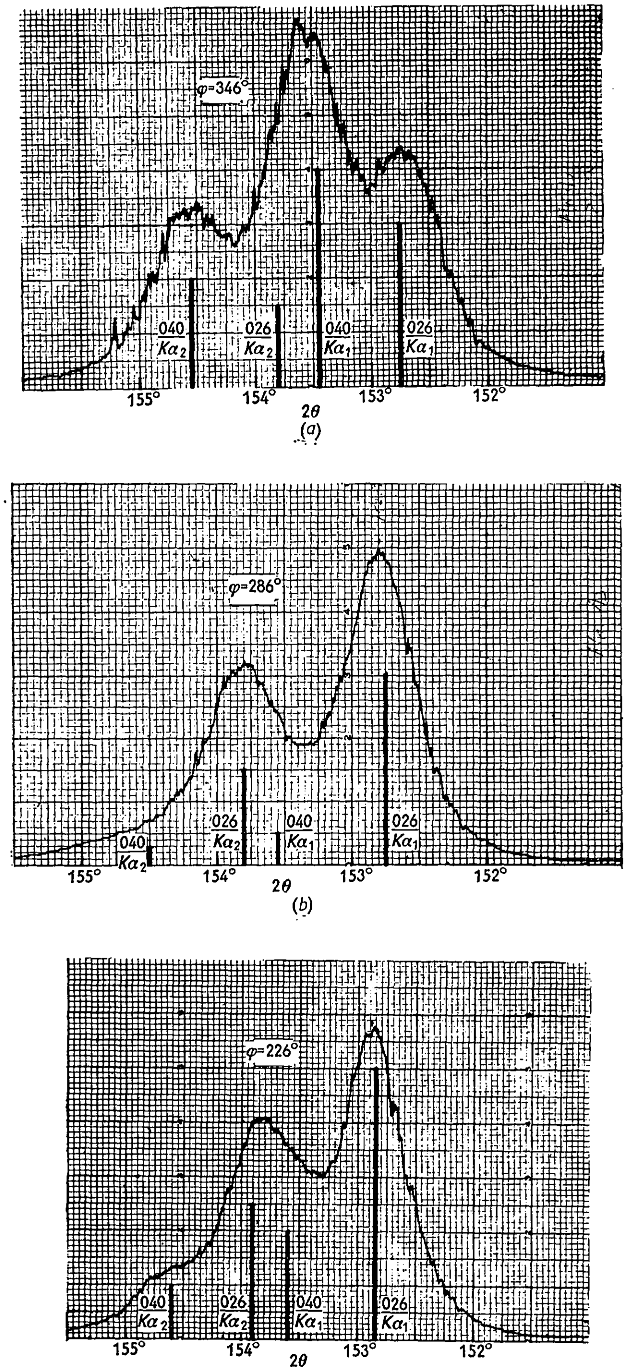

Fig. 2. The profiles of 040, 026 reflections at 60° intervals about [100] obtained with Co Kα, showing the effect of different proportions of twins at 55 °C. The heavy lines under the profiles indicate the relative heights of $K\alpha_1$ and $K\alpha_2$ peaks expected for the 3 twins in the proportions 4 : 2 : 1.

graphy (1952). This is illustrated in Fig. 3, where the relationship to the cell for a NiAs structure is also indicated. With this setting, the conditions limiting possible reflections are $0kl$: $k+l=2n$ and $hk0$: $h=2n$. With $z=4$, positions $4(c)$, $x\frac{1}{4}z$ *etc.* are demanded for both Mn and As.

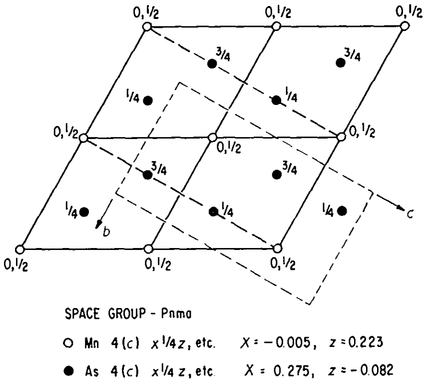

Fig. 3. The unit cell of the MnP form of MnAs in relation to the NiAs type cell.

Because of the composite character of the reflections with $k+l=2n$, the original intent was to use only the set of single reflections ($k+l=2n+1$) for the structure analysis. Accordingly, the photographic exposure times were set for best recording of this latter class of reflections. Subsequently, it became clear that it was necessary to utilize the other reflections also despite their composite nature. Hence, these too were then measured but not to the highest possible accuracy because of their generally high darkening. In some cases of overexposure for $K\alpha$, the $K\beta$ intensities were used instead. These intensities were important for establishing the scale factor, since a variety of solutions was possible on the basis of the non-overlapped reflections alone by using different combinations of scale factor and temperature factor.

The relationship between the intensities of the two classes of reflections can be deduced from a knowledge of the proportions of the twins and from intensity measurements of the overlapped reflections at *all* symmetrically equivalent positions. Thus, the average of the intensities at the latter positions weighted by the fractional occurrence of a given twin relates the composite reflections of that twin to its non-overlapped reflections ($k+l=2n+1$). The observed F^2 values of Table 1 are for the most prevalent twin, comprising approximately 60% of the volume.

Approximate parameter values were obtained by trial and error and these were refined by the least-squares program of Busing & Levy (1959) and also by a modified program (Kennicott, 1962) that allowed the sums of reflections to be considered, as was necessary for the reflections with $k+l=2n$. The latter program was written by P. Kennicott, who kindly made it available to us. As far as possible, the weights used were the inverse of the standard deviations determined from independent measurements of an F^2 (ΣF^2 for composite reflections). A good proportionality was found between σ and F^2 and this proportionality factor was applied to the other F^2 to give an estimate of their σ's.

Table 2. *Parameters from least-squares refinement*

(*a*) Final parameters using all F^2_{hkl}

	x	z	B	$\sigma(x)$	$\sigma(z)$	$\sigma(B)$
Mn	−0·0047	0·2229	1·10	0·0010	0·0022	0·13
As	0·2745	−0·0816	0·81	0·0016	0·0012	0·14
(*b*) Values using only F^2_{hkl} with $k+1=2n+1$						
Mn	−0·0061	0·2179	1·12	0·0007	0·0020	0·07
As	0·2799	−0·0813	0·86	0·0018	0·0006	0·09

The atomic parameters for a hexagonal NiAs type structure would be:

Mn $x=0,\ z=\frac{1}{4}$
As $x=\frac{1}{4},\ z=-\frac{1}{12}$

Three cycles of refinement sufficed for the set of single reflections (with $k+l=2n+1$), with the parameter values and standard deviations given in Table 2(*b*). The R value was 17·6% and the weighted R 10·7%, non-observed F^2 included. On the other hand, no refinement could be achieved when only the composite F^2 data were used. When both sets were combined, however, the refinement procedure seemed normal, and after 4 cycles the values in Table 2(*a*) were obtained. These gave R values of 15·6% for $k+l=2n+1$, 18·1% for $k+l=2n$, and 17·6% overall. The weighted R value, for reflections with $k+l=2n+1$, was 11·6%.

Although it seemed possible that the better parameters would be those obtained from refinement of non-overlapped reflections only, these produced some serious discrepancies for the overlapped data. For several reflections of high index, the calculated ΣF^2 was abnormally low, a situation not explainable by inaccuracy in the observed ΣF^2. Accordingly, the final parameters were taken to be those from refinement with all data, where such discrepancies are greatly diminished.

Comparison with neutron diffraction data

The details of the neutron diffraction studies will be published separately. We only wish to remark here that the structure resulting from the X-ray studies accounts quite well for the neutron powder diffraction patterns in the range of 40 to 125 °C, especially for what had appeared to be anomalous features. These included the occurrence of small new peaks and anomalous intensities for a NiAs type structure. This is particularly relevant to the question of the possibility of an antiferromagnetic state in this range of temperatures. With the satisfactory accounting for all of the neutron diffraction pattern by means of the orthorhombic structure, there is no ambiguity left about any magnetic scattering, and hence the phase between 40 °C and 125 °C appears to be paramagnetic.

The temperature dependence of intensities between 40 and 125 °C and the structure above 125 °C

Our X-ray investigation above 125 °C consisted only in establishing by precession photographs at 130 °C that the structure was again of a NiAs type, as had been indicated by our neutron diffraction data. More interesting, however, is the temperature dependence between 40° and 125 °C of the intensities of non-overlapped reflections characteristic of the orthorhombic MnP type structure. Integrated intensities of several reflections were measured, with a proportional counter, at various temperatures achieved by a specially constructed minature resistance furnace. Fig. 4 illustrates the rapid continuous decrease of the 301 reflection with temperature, compared to the overlapped 311, 302 reflections where the intensity, in fact oscillates slightly. It follows, assuming a homogeneous single phase to be present, that the 'orthorhombic distortion' diminishes in a continuous way as the temperature is increased to 125 °C. Such a behavior is characteristic of a Jahn–Teller distortion (Kanamori, 1960) from a more symmetrical structure, although it cannot be used by itself as proof of such an effect. Also, from the diffraction evidence only, the temperature dependence could be interpreted as due to the conversion from the MnP type structure to a MnAs type structure, which process is completed at 125 °C. The presence of a λ point in the specific heat

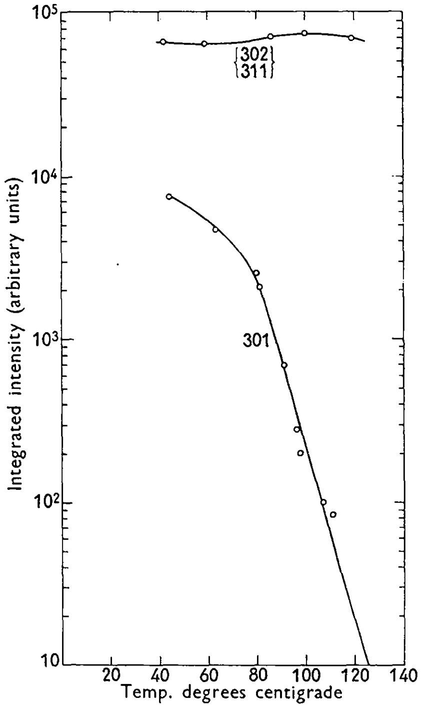

Fig. 4. Temperature dependence of intensities of MnAs.

at 125 °C would seem to make this latter interpretation less likely. Clearly, more work would be needed to clarify the structural changes occurring between 40° and 125 °C, but we do not contemplate any further investigation of this point.

Description of structure

The environments of Mn and As and the various bond distances are shown in Fig. 5 and 6. The distortion from a NiAs structure is similar to that in MnP although less in magnitude. The largest deviations from the NiAs parameters are for the *x* of As and the *z* of Mn. As a consequence, the trigonal prism of Mn atoms about an As is deformed in such a way that the Mn triangle closer to As is expanded while the other Mn triangle is contracted.

The distorted octahedral environment of a Mn is peculiar and one which we are unable to interpret. It appears definite that a short bond (2·52 Å) is formed parallel to [001] while the oppositely directed bond is the longest (2·61 Å) of the six bonds. The other four distances are not significantly different from each other nor from the Mn–As distance (2·58 Å) in the NiAs type structure at 39 °C. The configuration of neighbors about Mn cannot be readily understood in terms of crystal field effects or taken as evidence of a Jahn–Teller type distortion as has been suggested (Bean & Rodbell, 1962). Just as with other cases of structures of the MnP type, the reasons for the precise distortions in MnAs from more symmetrical coordinations about the atoms remain unclear.

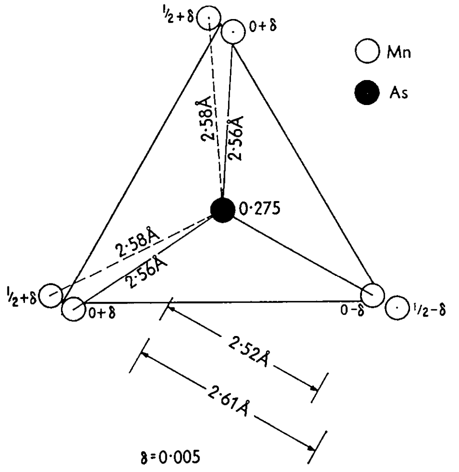

Fig. 5. Environment of Mn atoms around an As atom. The standard deviation of all distances is 0·19 Å.

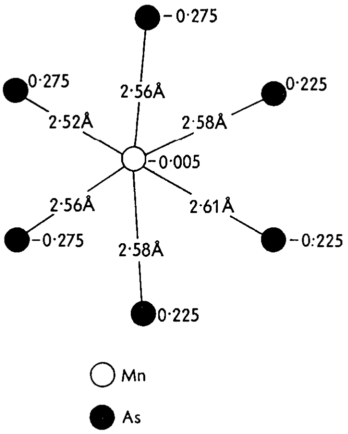

Fig. 6. Environment of As atoms around a Mn atom. The standard deviation of all distances is 0·019 Å.

We are very grateful for considerable help from H. Brandhorst in analysis of the diffraction data, from Mrs S. M. Richards in performing the least squares refinements, and from P. Kennicott for providing us with the special program for least squares refinement of overlapped data. We appreciate useful discussions with D. S. Rodbell and C. P. Bean who were responsible for our interest in the problem of MnAs structures.

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