

Table 1. *Crystal data of racemic and optically active pairs*

	Crystal system	Space group	Mols per cell <i>Z</i>	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Reference†
DL-Alanine	Ortho.	<i>Pna2</i> ₁	4	12.05	6.05	5.82	—	—	—	1
L-Alanine	Ortho.	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁ *	4	12.343	6.032	5.784	—	—	—	2
(±)- <i>trans</i> -1,2-Cyclohexanedicarboxylic acid	Mono.	<i>C2/c</i>	4	5.65	13.94	11.04	—	113°16'	—	3
(+)- <i>trans</i> -1,2-Cyclohexanedicarboxylic acid	Mono.	<i>C2</i> ₁	4	5.58	13.94	10.25	—	—	95°	4
(±)- <i>trans</i> -1,2-Cyclopentanedicarboxylic acid	Mono.	<i>C2/c</i>	4	9.25	6.65	12.18	—	100°38'	—	5
(+)- <i>trans</i> -1,2-Cyclopentanedicarboxylic acid	Mono.	<i>C2</i> ₁	4	9.24	6.64	12.04	—	—	96°	5

* The *a* and *b* unit cell dimensions have been interchanged.

† References: 1 Donohue (1950), 2 Simpson & Marsh (1966), 3 Benedetti, Coradini, Pedone & Post (1969), 4 Benedetti, Corradini & Pedone (1969), 5 Benedetti, Corradini & Pedone (1972).

forms of *trans*-1,2-cyclohexanedicarboxylic acid (Benedetti, Corradini, Pedone & B. Post, 1969; Benedetti, Corradini & Pedone, 1969). In this case it is possible to generate the structure of the optically active form assuming as conservative the *ab* plane of the racemic compound (containing isomorphous molecules) in the *C2/c* space group. The space group of the (+) form becomes *C2*₁ (see Table 1). The parameters of the conservative plane are only slightly modified in the (+) form as compared to the (±) ($\gamma_{\text{rac}} = 90^\circ$, $\gamma_{\text{op.act}} = 95^\circ$) but the fractional coordinates of the independent unit in the racemic compound are still very close to those of the refined optically active model.

By application of analogous considerations we have been able to solve the crystal structure of the optically active form of (+)-*trans*-1,2-cyclopentanedicarboxylic acid, once that of the (±) form was known.

A feature indicating the presence of a conservative layer of molecules in the two structures was that the parameters of the *ab* plane of a *C2*₁ space group (*c* unique axis) of the optically active form nearly coincide with the corresponding parameters of the *ab* plane of the racemic one (space group *C2/c*) (see Table 1) and the *0kl* reflexions were almost identical for the two compounds in the *C*-centered space groups. As a consequence, we expected no appreci-

able change in the fractional coordinates of the independent unit of the optically active structure as compared with those of the racemic one. This was verified and the resulting refined crystal structures of both forms will be published in detail elsewhere (Benedetti, Corradini & Pedone, 1972).

The study of the occurrence of this phenomenon in the structures of optically active and racemic forms is under further investigation in our laboratory.

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High pressure Mn₂As with Fe₂P-type structure. By W. JEITSCHKO and VANCLIFF JOHNSON, *Central Research Department,* E.I. du Pont de Nemours and Company Experimental Station, Wilmington, Delaware 19898, U.S.A.*

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Mn₂As has been prepared in a tetrahedral anvil high-pressure device at 65 kb. It has an Fe₂P-type structure with lattice constants *a* = 6.3627 (4) and *c* = 3.6784 (5) Å, space group *P6*₂*m*. The structure has been refined from single-crystal X-ray counter data. High-pressure Mn₂As is antiferromagnetic with Néel temperature 50 ± 10°K. Fe₂P-type Cr₂As is confirmed to be a high-temperature phase.

Introduction

Both Cr₂As (Nowotny & Årstad, 1938; Yuzuri, 1960) and Mn₂As (Nowotny & Halla, 1937; Yuzuri & Yamada,

1960) have been reported with the Cu₂Sb-type structure. Recently, Cr₂As was found with the Fe₂P-type structure at high temperature (Wolfsgruber, Boller & Nowotny, 1968). We also have prepared Fe₂P-type Cr₂As by quenching from high temperatures. We were not able to prepare Fe₂P-type Mn₂As in this way, but have found it at high pressures.

* Contribution No. 1890.

Table 1. Lattice constants for Cr₂As and Mn₂As phases with Cu₂Sb- and Fe₂P-type structure

Numbers given in parentheses are standard deviations in the last significant digit, but do not reflect variations in composition.

	Type	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> / <i>Z</i> (Å ³)	Reference
Cr ₂ As	Cu ₂ Sb	3.620	6.346	41.58	Nowotny & Årstad, 1938.
	Cu ₂ Sb	3.5923 (6)	6.3437 (12)	40.93	This work.
	Fe ₂ P	6.307	3.44 ₅	39.56	Wolfsgruber, Boller & Nowotny, 1968.
	Fe ₂ P	6.3407 (8)	3.4543 (6)	40.09	This work.
Mn ₂ As	Cu ₂ Sb	3.769	6.278	44.54	Nowotny & Halla, 1937.
	Cu ₂ Sb	3.78	6.25	44.65	Yuzuri & Yamada, 1960
	Fe ₂ P	6.3627 (4)	3.6784 (5)	42.99	This work.

Experimental

Mn₂As and Cr₂As were prepared by slowly heating stoichiometric mixtures of the elements (purity: 99.99%) to 700°C in evacuated silica tubes. The samples were afterwards held at 1100°C for a few hours and then quenched in water. Guinier-Hägg patterns of Cr₂As samples showed both Cu₂Sb and Fe₂P-type lines. Least-squares refinement, using high-purity KCl (*a* = 6.29310 Å) as internal standard, resulted in lattice constants listed in Table 1. Mn₂As samples prepared under these conditions gave Guinier-Hägg powder patterns of Cu₂Sb type. Compositions corresponding to Mn_{1.9}As and Mn_{2.1}As, quenched from 1100°C, both also showed Cu₂Sb-type X-ray patterns plus a few weak lines, none of which corresponded to an Fe₂P-type phase. Since at 1100°C Mn₂As is liquid, it was concluded that Fe₂P-type Mn₂As cannot be prepared as a high-temperature phase, corroborating the results obtained by Yuzuri & Yamada (1960). However, Cu₂Sb-type Mn₂As, formed at 700°C in silica tubes, was readily converted to the Fe₂P type by heating (BN-container) in a tetrahedral anvil apparatus (Bither, Gillson & Young, 1966) at 65 kb and 1200°C for 2 hours, with subsequent cooling to 1100°C and quenching to room temperature under pressure. Guinier-Hägg powder patterns of the product were indexed completely with an Fe₂P-type unit cell (Table 1).

The magnetic susceptibility between 4.2°K and room temperature was measured on powdered crystals with a vibrating-sample magnetometer. A maximum in the susceptibility at 50 ± 10°K suggests antiferromagnetic ordering below this temperature.

Structure refinement

A single crystal of high-pressure Mn₂As was investigated with a Buerger precession camera. The patterns confirmed Laue symmetry *6/mmm*. No systematic absences were found. Of the four possible space groups, only *P6̄2m* (*D*_{3h}⁶) is compatible with a structure similar to Fe₂P (Rundqvist & Jellinek, 1959). Single-crystal data were collected with an automated Picker diffractometer, graphite-monochromatized Mo *K*α radiation, scintillation counter, pulse-height discriminator, and the *θ*-2*θ* scan technique with scan speed 0.36° 2*θ*/min and scan angle 3.5° 2*θ*. The background was counted for 1 min at both sides of the scan. All reflections within one sextant up to (sin *θ*)/λ = 0.69 were measured and symmetry-equivalent reflections were averaged. No absorption correction was found necessary for the needle-shaped crystal (0.2 mm long and 0.045 mm in diameter). Finger's (1969) full-matrix least-squares program was used for the structure refinement. Atomic scattering factors were taken from Cromer & Mann (1968), corrected for anomalous

dispersion (Cromer & Liberman, 1970). The function $\sum_w (|KF_o - |F_c||)^2$ was minimized where *K* is a scale factor and *w* the weight based on counting statistics. An extinction correction in the form of $I_{corr} = I_{uncorr}/(1 - CI_{uncorr})$ was used (Zachariasen, 1963) where *C* = 1.5 × 10⁻⁵. Reflections for which this correction exceeded 25%, and reflections where *F_o* was less than the standard deviation were given zero weight and are marked with an asterisk in Table 2. Refinement with isotropic thermal parameters gave *R* = $\sum(|KF_o - |F_c||)/\sum F_o = 0.052$ for 87 observed reflections. Refinement with anisotropic thermal parameters reduced *R* substantially (*R* = 0.034; weighted *R* = 0.044). Variation of occupancies gave little further improvement (*R* = 0.033; weighted *R* = 0.041). The final parameters are listed in Table 3.

Discussion

The volume per formula unit (Table 1) is smaller for Fe₂P-type Cr₂As and Mn₂As than for the corresponding Cu₂Sb-type phases. Thus it is plausible that Fe₂P-type Mn₂As is stabilized by high pressure. Since, in general, high-temperature phases have the larger volume, it is surprising that Fe₂P-type Cr₂As is a high-temperature phase. However, one has to keep in mind that the volumes are determined at room temperature and pressure. The relative volumes may, therefore, be different at high temperatures and pressures owing to differences in thermal expansion and compressibilities of the two structures.

In Table 4, interatomic distances of Mn₂As with the Fe₂P- and Cu₂Sb-type structures are compared. Nearest-neighbor coordinations are similar in the two structures. In both, As has 9 near Mn neighbors (coordination polyhedra, though, are different) and in both there are two kinds of Mn atoms - one with tetrahedral and one with

Table 2. Observed and calculated structure factors of Mn₂As with Fe₂P-type structure

Reading from left to right, the columns contain the values *hkl*, *F*_{obs}, *F*_{calc}.

000	0	2469*	001	304	247	002	1471	1522*	403	25	21	
100	0	91*	101	189	184	102	0	**	503	320	314	
200	141	141	201	922	946	202	109	102	6*3	114	117	
300	1042	999	301	191	152	302	739	762	113	439	435	
400	340	328	401	50	56	402	205	217	213	211	211	
500	371	359	501	435	440	502	249	274	313	184	179	
600	210	206	601	134	136	602	176	180	413	230	233	
700	186	182	701	253	237	702	295	281	513	205	204	
110	312	315	111	792	793	112	406	428	223	125	100	
210	605	619	211	533	529	212	244	248	303	387	398	
310	311	318	311	272	279	312	425	433	423	191	200	
410	944	940	411	341	343	412	181	177	313	106	120	
510	231	228	511	322	325	512	134	145	004	188	710	
610	190	176	611	297	289	612	409	417	104	0	31*	
720	499	502	721	135	140	722	146	152	204	56	52	
820	213	215	821	612	631	822	719	729	3	4	424	416
420	285	283	421	194	301	422	361	365	404	84	70	
520	443	431	521	173	176	522	319	341	114	180	190	
620	162	155	621	216	212	622	84	78	214	203	194	
320	495	424	321	136	139	322	120	126	314	153	160	
430	98	101	431	156	156	432	152	146	224	245	258	
530	95	98	531	162	161	532	550	540	324	73	64	
440	456	435	441	418	418	442	134	129	005	70	42	

Table 3. Final occupational, positional and thermal parameters of the high-pressure phase Mn₂As

Vibrational parameters ($\times 10^4$) are defined through $T = \exp(-\sum_i \sum_j h_i h_j \beta_{ij})$. Numbers in parentheses are estimated standard deviations in the last significant digits.

Atom ($P\bar{6}2m$)	Occupation	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn(1) in 3g	1	0.5904 (5)	0	$\frac{1}{2}$	92 (8)	90 (11)	208 (19)	$\frac{1}{2}\beta_{22}$	0	0
Mn(2)	3f	0.99 (2)	0	0	64 (8)	56 (11)	471 (26)	$\frac{1}{2}\beta_{22}$	0	0
As(1)	2c	0.99 (1)	$\frac{1}{2}$	0	61 (6)	β_{11}	148 (14)	$\frac{1}{2}\beta_{22}$	0	0
As(2)	1b	0.92 (3)	0	$\frac{1}{2}$	100 (10)	β_{11}	279 (29)	$\frac{1}{2}\beta_{22}$	0	0

square-pyramidal As coordination. A significant difference is the large number of Mn nearest and second nearest neighbors for Mn(1) in the Fe₂P-type structure. This is plausible since, in general, structures with higher coordination numbers are stabilized by high pressure.

Table 4. Interatomic distances in Fe₂P-type high-pressure Mn₂As

Standard deviations are all less than 0.004 Å. All distances less than 3.65 Å are given. For comparison interatomic distances of Cu₂Sb-type Mn₂As as determined by Nowotny & Halla (1937) are also given.

Fe ₂ P-Type		Cu ₂ Sb-Type	
Mn(1)···1As(2)	2.606	Mn(2c)···1As	2.54
4As(1)	2.662	4As	2.70
2Mn(2)	2.841	4Mn	2.80
4Mn(2)	2.926	[4Mn	3.41]
[4Mn(1)	3.334]		
Mn(2)···2As(1)	2.429	Mn(2a)···4As	2.51
2As(2)	2.432	4Mn	2.67
2Mn(2)	2.756	4Mn	2.80
2Mn(1)	2.841		
4Mn(1)	2.926		
As(1)···3Mn(2)	2.429	As······4Mn	2.51
6Mn(1)	2.662	1Mn	2.54
		4Mn	2.70
As(2)···6Mn(2)	2.432		
3Mn(1)	2.606		

The occupancy of 0.92 ± 0.03 for the As(2) position obtained from the least-squares refinement could be due to vacancies or to partial substitution of As with Mn. The latter is more likely in a phase prepared under high pressure. However, this small deviation from full occupancy should not be weighted too strongly since systematic errors in the data might also cause this result.

Analysis of the vibrational ellipsoids shows that the decrease in R from 0.052 to 0.034 is due to anisotropic vibration of only Mn(2). The vibrational ellipsoids of the other three atoms show only little deviations from corresponding spheres. This result is possibly significant since in TiFeSi (a distorted Fe₂P structure; Jeitschko, 1970) one of the largest displacements from the ideal Fe₂P-type is the x coordinate of the Fe atoms in 8c. This coordinate corre-

sponds to the direction of largest displacement in the thermal vibration of Mn(2). According to the theory of diffusionless phase transformations developed by Cochran (1969), anisotropic vibrations with large amplitudes occur in the high-temperature phase of compounds which transform to a lower-symmetry structure upon cooling. Our magnetic data show only a smooth transition at $\sim 50^\circ\text{K}$ which we have interpreted as an antiferromagnetic transition; however, this may also be accompanied by a structural transformation. The Néel temperature for Fe₂P-type Mn₂As is much lower than for Cu₂Sb-type Mn₂As ($T_N = 573^\circ\text{K}$; Yuzuri & Yamada, 1960) but much closer to that of Fe₂P-type Mn₂P ($T_N = 103^\circ\text{K}$; Yessik, 1968). This suggests that the magnetic structure of Fe₂P-type Mn₂As might be similar to Mn₂P.

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