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Manganese Monoarsenide

Thermodynamic Properties in the Range 5 to 700°K and Transition Behavior

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The heat capacity of MnAs has been measured in the range 5 to 700°K by adiabatic shield calorimetry. Values for the entropy $(S°-S_0°)$, enthalpy $(H°-H_0°)$, and Gibbs energy function $[-(G°-H_0°)/T]$ have been calculated and are presented in tabular form. The earlier known transitions about 316°K and 393°K have been studied in detail. The former is a combined ferro-to-paramagnetic and structural transition with an entropy increment of 12.8 J $mole^{-1}$ $°K^{-1}$. The heat capacity does not become infinite in the transition region and X-ray investigations show the presence of two phases in the sample, gradually changing in amounts in the range 315 to 320°K. The 393°K transition is very small compared to the 316°K transition and the decrease in heat capacity across the former transition with increasing temperature is occasioned by a smaller dilation contribution above 393°K. The sum of the expected contributions to the heat capacity is smaller than that observed, probably due to excitations from low to high spin states in manganese. Thus, the 316°K transition does not imply complete randomization of the spins. The $\Delta Sf°$ and $\Delta Gf°$ are 10.0 J $mole^{-1}$ $°K^{-1}$ and −59.9 kJ $mole^{-1}$ $°K^{-1}$ at 298.15°K.

The unusual properties of manganese monoarsenide have occasioned a number of investigations. So far, however, its thermodynamic properties have not been thoroughly explored. Only some heat capacity data in the transition range between ferro- and paramagnetism and a determination of its enthalpy of formation at 298°K have been reported. Heat capacity measurements extending from low temperatures to well above the transitions are obviously needed for further evaluation of the changing properties. In a theoretical study Bean and Rodbell [1] explored the possibility of a first-order

transformation from a ferro- to paramagnetic state. They found that such a transformation was indeed possible if the exchange interactions varied sufficiently rapidly with the lattice dimensions of an adequately compressible lattice, and concluded that this was the case for the transition in MnAs at about 316°K. The metal to non-metal distance is unusually large in manganese pnictides and chalcogenides due to the unpaired spins,[2] and the sudden contraction in volume indicated to us that changes occur in the number of unpaired spins which should manifest themselves in the thermal properties.

Early magnetic measurements [3,4] on manganese monoarsenide showed it to be ferromagnetic below about 316°K. The relationship between magnetic and thermal properties was studied by Bates,[5] who determined the heat of transformation. He concluded that the heat capacity increased rapidly when the substance changed from the ferromagnetic to the paramagnetic state around 316°K and that the transformation was not completed at the critical point, but had only reached a "particular stage". The properties of MnAs were studied further by Guillaud [6–9] by several methods. For an alloy containing 49.54 atomic % As, the extrapolated magnetic moment was 3.40 μB. Heat capacity and relative electric resistivity measurements were carried out in the transformation region. Dilatometric data were also obtained which showed a sudden volume contraction of the order of 2.5 % at 318°K on heating, and a corresponding dilation at 307°K on cooling. His X-ray data confirmed the results of Oftedal [10] and of Nowotny and Halla [11] that the structure of MnAs was of the hexagonal NiAs-type, and not of the orthorhombic MnP-type as reported by Fylking.[12] Magnetic measurements [13–15] showed a slight increase in susceptibility in the range up to 393°K, which was attributed to antiferromagnetism by Meyer and Guillaud (*cf.* Guillaud [9]), and shown to be accompanied by a thermal anomaly. In the range 400 to 650°K the susceptibility was shown to follow the Curie-Weiss law ($\theta_p \approx 283$°K) and indicating $\mu_{eff} = 4.95$ μB.

A more detailed study of the lattice constant changes in MnAs by Willis and Rooksby,[16] showed a contraction of the *a*-axis near 313°K of about 2 %, in agreement with the results by Guillaud. In the range 313 to 573°K the *a*- and *c*-axis increased regularly except for an inflection in both around 410°K. The results were discussed in terms of a first-order transition from ferro- to antiferromagnetism and a second-order one from antiferro- to paramagnetism. A thermodynamic exchange-inversion theory worked out by Kittel [17] to explain the transitions from ferro- (or ferri-) to paramagnetism in special substances, like MnAs, chromium-substituted Mn_2Sb, and Dy, leaned upon the importance of the exchange magnetoelastic energy.

The possibility of a transition from ferro- to antiferro- and then to paramagnetism on heating MnAs was questioned from the outset (see discussion section, Ref. 9) and neutron diffraction work by Bacon and Street [18] showed no indications of antiferromagnetism in the 316 to 393°K region. Nevertheless, Meyer and Taglang [19] after having measured the magnetocaloric effect for MnAs from about 293 to 450°K reassert that the compound is antiferromagnetic in the range 316 to 393°K.

In a work by Basinski and Pearson [20] the 316°K transition was studied under the microscope by cinematography and also by induction measurements.

It appeared to be discontinuous, diffusionless, and non-martensitic. Transformation of individual grains took place within 5×10^{-7} sec, which was the resolving time of the apparatus. Expansion of the a-axis on cooling produces cracks, dividing the crystal into rod-like subgrains. After further discussion [21] it was concluded that the structural transition at 316°K is first order and the magnetic transition is second order. High dispersion X-ray photographs of MnAs in the region 316 to 393°K taken by Kornelsen [22] showed that the structure was not hexagonal in this region but consistent with an orthorhombic cell, ($a=5.72_4$, $b=3.66_8$, $c=6.367$ Å at 324°K). The departure from hexagonal structure is greatest just above 313°K and decreases as the temperature approaches 393°K. Further work by Wilson and Kasper [23] showed the structure to be of the MnP-type with distorted octahedral environment of the Mn-atoms (one As at 2.51 Å, four at 2.58 Å and one at 2.61 Å). They thought that the configuration could not be readily understood in terms of crystal field effects, or taken as an indication of a Jahn-Teller type distortion as had been suggested by Bean and Rodbell.[1]

The magnetic transition around 316°K differs from the usual ferro- to paramagnetic ones in being discontinuous. This led Bean and Rodbell [1] to consider the theoretical possibilities for a first order change, and the theory motivated DeBlois and Rodbell [24] to extend the earlier measurements of Meyer and Taglang [25] and Rodbell and Lawrence [26] of the variation in Curie temperature as function of field strength and pressure up to 110 kOe and one kbar. The data were shown to substantiate the application of the Bean-Rodbell theory to the MnAs transition. In a more recent study of the temperature-pressure stability range of the hexagonal and orthorhombic MnAs phases by Goodenough and Kafalas [27] the volume dependence was considered due to electron re-arrangements associated with a high-spin to low-spin transition. Since the sharpness of the transition could not be accounted for by variations in crystal field splitting with volume it was suggested that the band width of the $t\pm$ orbitals is decreasing with increasing volume through the maximum band width for spontaneous band ferromagnetism.

The temperature-pressure relationships of the MnAs phases studied by Grazhdankina and Bersenev [28] accorded reasonably well with the results of Goodenough and Kafalas.[27] They also found a transition in the high pressure (MnP-type) phase from para- to antiferromagnetism. In another study Grazhdankina and Burkhanov [29] determined the elastic properties of MnAs in the range from 290 to 460°K and found no change at the 316°K transition, but a decrase in compressibility to about one third in the range 400 to 440°K. The data were interpreted in favor of a transition from ferro- to antiferromagnetism at 316°K and a Néel temperature of 400°K for the antiferromagnetic phase.

EXPERIMENTAL

A. Samples

Manganese arsenides were prepared by reacting the pure elements in evacuated and sealed quartz tubes. Manganese metal flakes with a stated purity of 99.995 % Mn were supplied by L. Light and Co., England. The reported impurities were 5 ppm of Mg and

Si. The flakes were heated with dilute nitric acid to remove surface oxidation products and afterwards degassed *in vacuo* (10^{-5} torr) at 700°C for 2 h. The 99.9999 % arsenic was also supplied by L. Light and Co. It was reported to contain less than 0.3 ppm Pb, and Ca, Cu, Mg, S, and Si in amounts less than 0.1 ppm. The manganese flakes were fragmented and subsequently crushed in an agate mortar before use.

In one series the reaction between manganese and arsenic was carried out at 900°C. After two days at this temperature all samples were cooled to room temperature and crushed to powder. They were then tempered at 700°C for one week and quenched in water. Other series were similarly reacted and tempered at 700 and 500°C, respectively.

For X-ray and microscopic studies a series of samples with compositions $MnAs_x$ ($x=0.85$, 0.90, 0.95, 0.99, 1.00, 1.02, 1.05, 1.10, 1.15, and 1.20) were prepared. In all those containing more arsenic than the stoichiometric ratio 1:1, condensation of elemental arsenic was observed. By weighing the condensed As in $MnAs_{1.02}$, for example, the composition of the arsenide was calculated to be $MnAs_{0.998}$. Several experiments were carried out to see if higher arsenides might form at lower temperatures, but surplus arsenic over the 1:1 ratio was then always observed. The lattice constants of the MnAs-phase were found to be constant within the limits of precision for all samples quenched from 500°C; $a=3.720\pm0.001$ Å, $c=5.705\pm0.001$ Å. Increasing amounts of a lower arsenide were seen in photographs of samples containing more manganese than $MnAs_{0.98}$. Thus, manganese monoarsenide is considered to be very closely stoichiometric, with no range of homogeneity observable after quenching from 500°C, in contrast to the observations by Guillaud [6] of a homogeneity range from 47 to 50 atomic % As.

X-Ray powder photographs of the samples were taken in 80 mm diameter Guinier cameras with Cu$K\alpha_1$ radiation. ($\lambda=1.54051$ Å) and KCl as a calibration substance ($\alpha_{20}=6.2919$ Å) according to Hambling.[30] A 114.6 mm diameter Debye Scherrer camera was used for taking photographs in the range 20 to 65°C. A GE horizontal goniometer with heating stage was used in other series of experiments. Metallographic investigations were made with a Reichert MeF microscope with heating stage.

For the calorimetric measurements a 160 g sample of $MnAs_{1.00}$ was prepared as outlined above in five smaller batches. The reaction temperature was 900°C. The smaller batches were crushed, mixed and transferred to a larger ampoule for heat treatment at 700°C. After one week the heating was discontinued and the sample cooled to room temperature during a period of about 8 h.

B. Calorimetric technique

1. *5 to 350°K, University of Michigan.* The Mark II cryostat and adiabatic method employed have been described.[31] A gold-plated copper calorimeter (W-42) with a volume of 93 cm^3 was used. Helium gas was added (70 torr at 300°K) to improve thermal equilibration. The calorimeter was surrounded by a shield system provided with automatic temperature control. Temperatures were measured with a capsule-type platinum resistance thermometer (A-5) located in a central well in the calorimeter.

2. *300 to 700°K, University of Oslo.* The calorimetric apparatus and measuring technique have been described.[32] The calorimeter was intermittently heated, and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed quartz tube of about 50 cm^3 volume, tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer.

3. *Calibrations.* The platinum resistance thermometer for the low-temperature calorimeter had been calibrated by the U. S. National Bureau of Standards, and that for the high-temperature calorimeter locally, at the ice, steam, and zinc points. Temperatures are judged to correspond to IPTS (1948) within 0.02°K from 4 to 300°K, and within 0.05°K above this temperature. Energy inputs were measured with reference to instruments calibrated by the Bureau of Standards.

The heat capacity of the empty calorimeters was determined in separate series of experiments. It usually represented from 17 to 25 % of the total in the case of the low-temperature calorimeter, and about 50 % in the case of the high-temperature calorimeter.

Small corrections were applied for temperature excursions of the shields from the calorimeter temperature and for "zero drift" of the calorimeter temperature. Further

Table 1. Heat capacity of manganese monoarsenide.[a] Series I–X: Data from cryogenic calorimeter. Series XI–XXII: Data from high-temperature calorimeter.

$\bar{T}$	C_p	$\bar{T}$	C_p	$\bar{T}$	C_p
Series I		10.49	0.268	Series X	
		12.06	0.385		
104.69	35.43	13.37	0.531	298.17	70.00
112.27	37.92	14.76	0.741	304.79	73.18
121.46	39.58	16.28	1.008	309.55	76.36
130.25	41.47	17.93	1.360	311.65	78.07
137.59	42.91	19.61	1.778	312.82	79.96
144.71	44.20	21.51	2.314	313.93	90.92
152.64	45.53	23.94	3.079	314.76	165.4
161.36	46.88	27.02	4.167	315.21	378
169.84	48.13			315.47	456
178.12	49.27	Series VI		315.63	1290
186.22	50.36			315.74	890
		23.31	2.874	315.86	880
Series II		26.07	3.824	316.01	710
		29.18	4.983	316.23	620
177.97	49.24	32.27	6.268	316.45	399
186.08	50.33	33.31	6.699	316.90	192
194.10	51.38	36.22	7.975	317.55	128.2
202.64	52.51	39.34	9.381	318.45	92.2
211.61	53.65	42.34	10.761	319.60	68.95
220.41	54.80	45.17	12.125	321.37	57.24
229.05	56.02	48.74	13.816	323.62	56.90
237.53	57.15	53.15	15.92	326.63	56.90
245.86	58.35	54.79	16.67		
254.03	59.61	59.37	18.82	Series XI	
262.60	61.07	63.55	20.76		
		68.05	22.72	305.84	71.13
Series III		73.28	24.85	308.39	73.28
		79.01	27.14	310.86	79.74
ΔH detns. A		85.65	29.66	313.13	96.31
273.68	63.18	93.43	32.18	315.06	131.58
282.56	65.19	101.92	34.64	316.42	148.46
				317.83	205.46
Series IV		Series VII			
				Series XII	
ΔH detns. B		*ΔH* detns. D			
		ΔHt detns. E		330.15	57.48
268.57	62.13			342.83	57.47
276.94	63.85	Series VIII		355.37	57.44
				367.74	57.76
ΔHt detns. C		*ΔHt* detns. F		379.95	58.17
				387.29	58.45
325.26	57.03	Series IX		393.12	58.45
335.03	56.90			398.89	56.29
343.15	57.36	*ΔHt* detns. G		407.63	55.01
				419.30	54.57
Series V		322.31	57.49	430.90	54.63
		328.68	56.94	442.45	54.44
6.00	0.105	336.64	56.86	453.94	54.23
6.97	0.100	344.59	56.94	465.35	54.53
8.65	0.163				

Table 1. Continued.

476.69	54.62	Series XVI		Series XX	
485.27	54.55				
496.40	54.83	384.81	58.00	318.29	84.13
507.46	54.77	389.09	58.66	319.82	65.03
518.49	54.73	391.86	60.16	321.51	57.30
529.43	54.88	394.66	59.21	323.25	56.84
540.31	55.07	397.49	57.31	325.00	56.72
551.13	55.25				
		Series XVII		Series XXI	
Series XIII					
		316.05	613	554.83	55.33
314.01	107.92	316.20	649	568.30	55.47
315.50	281.7	316.35	648	581.72	55.59
316.45	300.6	316.50	638	595.09	55.75
		316.67	531	608.41	55.97
Series XIV		316.87	409	621.68	56.14
		317.23	305	634.90	56.27
316.63	239.26	317.98	130.0	648.07	56.33
317.72	239.35			659.68	56.51
320.09	118.35	Series XVIII		672.76	56.70
324.69	57.75			685.79	56.87
315.43	150.17	285.05	66.17		
315.91	219.19	289.21	67.02	Series XXII	
319.09	128.45	294.69	68.93		
				380.97	57.93
Series XV		Series XIX		385.44	58.45
				387.74	58.84
315.17	146.49	318.80	105.50	390.03	59.18
315.55	259.40	377.84	57.63	392.95	60.50
315.79	440.59	384.97	58.13	299.45	70.24
316.03	471.29	387.79	58.44	310.14	95.34
		390.60	58.77	315.57	589
		393.39	59.46		

[a] Units: J, mole, °K. 1 mole MnAs≙129.86 g.

small corrections were applied for differences in amounts of indium-tin solder, helium gas, and Apiezon-T grease for the low-temperature calorimeter and for differences in mass of the quartz containers for the high-temperature calorimeter. The mass of sample used was 157.352 g in the low-temperature calorimeter and 157.640 g in the high-temperature calorimeter.

RESULTS AND DISCUSSION

A. Heat capacities and thermodynamic properties

The measured heat capacities are presented in Table 1 and Fig. 1 for one mole of manganese monoarsenide, equal to 129.86 g. Temperature increments of the measurements can usually be deduced from the difference in adjacent mean temperatures. When necessary, corrections have been applied for the finite temperature increments to obtain the limiting value of $\Delta H/\Delta T$. The measurements are considered to have a probable error of about 5 % at

5°K, 1 % at 10°K, less than 0.1 % in the region 25 to 350°K for the low-temperature calorimeter, and 0.3 % above 300°K for the high-temperature calorimeter.

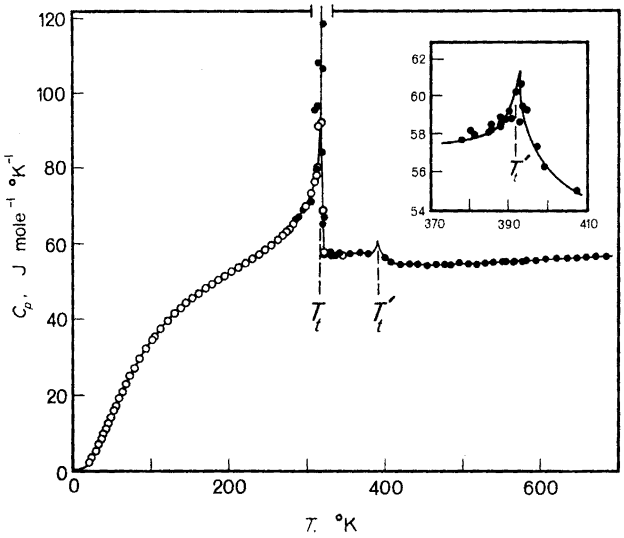

Fig. 1. Heat capacity of MnAs.

Two λ-type transitions are observed, one with a maximum of about 1300 J mole^{-1} °K^{-1} at 315.6°K and a much smaller one with maximum of about 60 J mole^{-1} °K^{-1} at 393.5°K. Earlier heat capacity data by Bates,[5] Guillaud,[6]

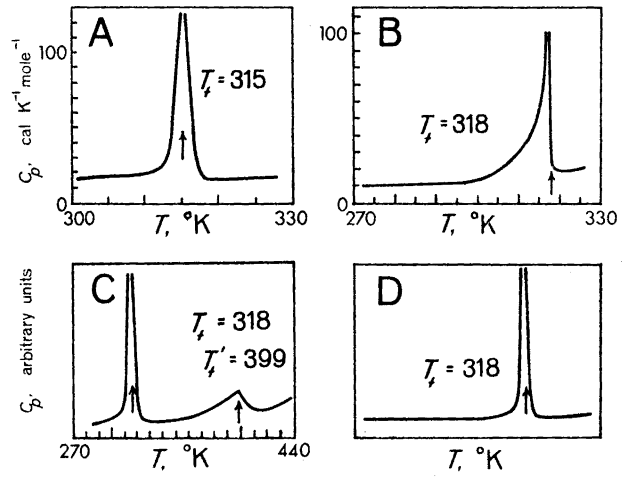

Fig. 2. Earlier heat capacity results on MnAs. A represents data by Bates,[5] B by Guillaud,[6–9] C by Meyer and Taglang,[15] and D by Basinski, Kornelsen and Pearson.[21]

Meyer and Taglang,[15] and Basinski, Kornelsen and Pearson [21] are shown in Fig. 2. They are in qualitative agreement with the results obtained here. Estimates of the enthalpy and entropy of the 316°K transition are presented in Table 2.

Table 2. Enthalpy and entropy of the 316°K transition in manganese monoarsenide.[a]

Detn. Designation	No. of Detns.	T_1	T_2	$H_{T_2}-H_{T_1}$	$H_{320}-H_{280}$
C, (Series IV)	6	281.30	320.01	3728	3811
E, (Series VII)	11	288.69	320.94	3284	3797
F, (Series VIII)	11	292.26	320.03	2997	3807
G, (Series IX)	19	288.74	319.93	3230	3809
Average value				$H_{320}-H_{280}$ =	3806
− Lattice contribution [b]				$H_{320}-H_{280}$ =	−1891
					1915
+ Excess below 280°K [b]				$\Delta(H_{280}-H_{70})$ =	1355
				ΔHt =	3270
				ΔSt =	12.8
T_t = 315.6					

[a] Units: J, mole, °K. 1 mole MnAs ≙ 129.86 g.
[b] After adjustment for estimated dilation and conduction electron terms, *cf.* text.

Enthalpy-type determinations in Table 1 (A in Series III, B in Series VI and D in Series VII) provide a test of the heat capacity measurement and integration procedures. The enthalpy increments thus determined accord with corresponding values derived from the smoothed heat capacity curve within 0.02 %.

Values of the heat capacity C_p, entropy $S°$, enthalpy $(H°-H_0°)$ and Gibbs energy function $[-(G°-H_0°)/T]$ are given for selected temperatures in Table 3. They were obtained by appropriate computer evaluation of the polynomials representing the heat capacity data and extrapolations below 5°K, assuming a linear C_p/T^2 *versus* T relationship down to 0°K. The probable errors in the tabulated values of these functions are judged to be less than 0.1 % above 100°K. Additional digits beyond the significant ones are given in the table because of their importance on a relative scale and for interpolation purposes. The contributions of nuclear spin and isotopic mixing to the entropy and Gibbs energy function have not been included.

B. Transitions

During the last years several theories have been proposed regarding the mechanism of the transitions around 316 and 393°K. For all of these, the energetic changes are of crucial importance and we shall therefore try to

Table 3. Thermodynamic properties of manganese monoarsenide.[a]

T	C_p	$S^\circ - S_0^\circ$	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$
5	0.100	0.033	0.096	0.017
10	0.222	0.126	0.770	0.046
15	0.782	0.301	3.054	0.096
20	1.879	0.665	9.489	0.188
25	3.443	1.243	22.63	0.339
30	5.326	2.033	44.45	0.552
35	7.427	3.012	76.26	0.833
40	9.682	4.151	118.99	1.176
45	12.037	5.422	173.3	1.573
50	14.418	6.816	239.4	2.029
60	19.12	9.862	407.2	3.075
70	23.54	13.146	620.8	4.276
80	27.53	16.56	876.6	5.598
90	31.05	20.01	1169.8	7.008
100	34.14	23.44	1496.2	8.481
110	36.85	26.83	1851	9.996
120	39.25	30.14	2232	11.535
130	41.40	33.36	2636	13.092
140	43.33	36.50	3059	14.652
150	45.09	39.56	3502	16.21
160	46.68	42.52	3961	17.76
170	48.16	45.40	4435	19.30
180	49.53	48.18	4924	20.83
190	50.85	50.90	5425	22.34
200	52.14	53.54	5940	23.84
210	53.43	56.12	6468	25.31
220	54.76	58.63	7008	26.77
230	56.12	61.10	7565	28.21
240	57.52	63.51	8134	29.63
250	58.99	65.89	8715	31.03
260	60.60	68.23	9314	32.42
270	62.42	70.56	9929	33.79
273.15	63.06	71.28	10120	34.22
280	64.56	72.84	10560	35.14
290	67.20	75.17	11220	36.48
298.15	70.17	77.07	11780	37.56
300	70.92	77.53	11910	37.81
320	64.43	85.40	14380	40.48
340	57.07	88.88	15520	43.23
360	57.45	92.13	16650	45.86
380	58.03	95.23	17810	48.37
400	55.94	98.24	18970	50.79
420	54.68	100.9	20070	53.10
440	54.43	103.5	21170	55.35
460	54.48	105.9	22250	57.49

Table 3. Continued.

480	54.56	108.2	23350	59.54
500	54.68	110.4	24440	61.55
550	55.19	115.6	27180	66.23
600	55.86	120.5	29960	70.54
650	56.44	125.0	32760	74.56
700	57.03	129.2	35600	78.32

[a] Units: J, mole, °K. 1 mole MnAs≙129.86 g.

estimate the lattice contribution to the heat capacity in order to find the excess thermodynamic properties.

In the temperature region up to 100°K one can estimate the lattice heat capacity at constant volume from the experimental value, C_{exp}, by subtracting (1) the dilation contribution, C_d, (2) the conduction electron contribution, C_e, and (3) the magnetic spin wave contribution, C_m; *i.e.*,

$$C_v = C_{exp} - C_d - C_e - C_m$$

Combination of the available expansion data below room temperature [33] with the extrapolated (constant) compressibility allows estimation of the dilation contribution in accordance with the thermodynamic relationship

$$C_p - C_v = C_d = (\beta^2/\varkappa)\ VT$$

where β is the volume expansion coefficient, $\varkappa$ the isothermal compressibility and V the molar volume. The dilation contribution is exceedingly small due to the cancellation of the thermal expansion by the magnetic contraction. MnAs is a metallic conductor [34] ($\varrho = 1.7 \times 10^{-4}$ ohm cm at 273°K) but complete data for determining the conduction electron contribution are not available. The contribution was tentatively set equal to that calculated for MnSb on the basis of Hall coefficient measurements [35,36] $C_e \approx 1.5 \times 10^{-3}\ T$ J mole^{-1} °K^{-2}.

Finally, the spin-wave contribution was calculated from the equations given by Dyson [37] as

$$C_m \approx 0.47 \times 10^{-3}\ T^{3/2}\ \text{J mole}^{-1}\ \text{°K}^{-5/2}$$

Debye θ values were calculated from the deduced heat capacity at constant volume below 80°K and extrapolated to higher temperatures ($\theta = 310$°K for $T > 150$°K) by comparison with $Ni_{0.95}Se$.[38] C_m can then be estimated by subtracting $C_v + C_e + C_d$ from the experimental data.

The results are shown in Fig. 3 for different alternatives for the dilation contribution. One is based upon the compressibility and expansion data by Grazhdankina and Burkhanov,[29] another on the same compressibility data and expansion data by Willis and Rooksby.[16] In addition, the contribution in the high temperature region was estimated according to Nernst and Lindemann [39] as

$$C_d = A(T/T_f)\ C_p^2$$

where $A = 0.00255$ mole °K J^{-1} and the melting temperature, $T_f = 1208$°K.[40] The sum of $C_v + C_e + C_d$ is apparently not large enough to explain the observed

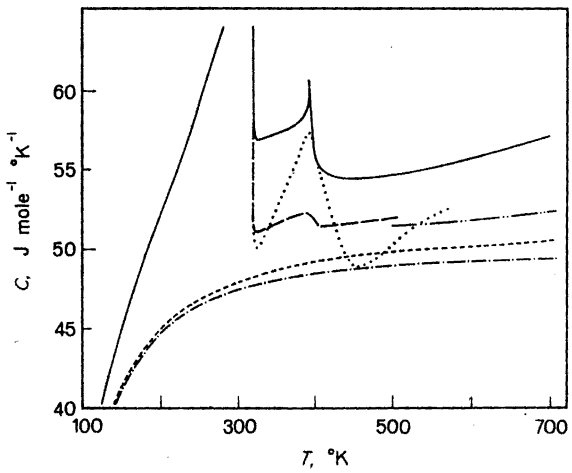

Fig. 3. Tentative resolution of the heat capacity of MnAs. ——— represents experimental heat capacity, C_{exp}; —·—·—·— represents heat capacity at constant volume, C_v; - - - - - represents C_v plus conduction electron contribution, C_e; — — — — represents C_{exp} minus dilation contribution, C_d calculated from data by Grazhdankina and Burkhanov;[29] ····· represents $C_{exp}-C_d$ taking values of $\varkappa$ from Ref. 29 and β from Ref. 16; —··—··— represents $C_{exp}-C_d$ according to Nernst and Lindemann.[39]

heat capacity in the high temperature region, and magnetic (3*d*-electron) contributions are therefore probably present. Very accurate expansion data are obviously needed to ascertain more exactly the dilation contribution in the transition regions.

The enthalpy and entropy increments of the ferromagnetic transition were calculated by assuming it to be complete at 320°K. The resulting values are $\Delta St = 12.8$ J mole^{-1} °K^{-1} and $\Delta Ht = 3270$ J mole^{-1}. The enthalpy value earlier reported by Bates [5] is $\Delta Ht = 970$ J mole^{-1}, while the heat capacity measurements by Guillaud results in the value $\Delta Ht = 1300$ J mole^{-1} according to De Blois and Rodbell.[24] These values — which do not include contributions arising below 300°K (1760 J mole^{-1}) — are of the correct order of magnitude.

Assuming now that three (*i.e.* 3.4) spins on the manganese atoms become completely randomized above the 316°K transition the magnetic increment should be

$$\Delta St_m = R \ln (2S+1) \sim 12.0 \text{ J mole}^{-1} \text{ °K}^{-1}$$

which is in good agreement with the observed value. It was noted by Guillaud, that the magnetization of MnAs suddenly disappeared around 318°K instead of following the Brillouin function behavior. Thus, if one subtracts magnetic disorder entropy acquired up to the transition temperature from the expected total, a value for the magnetic "latent heat" might be obtained. According to Bean and Rodbell [1] the reduced magnetization (B_j) at the transition temperature is $B_j = (\sigma_{Tc}/\sigma_0) = 0.65$ and thus according to the Brillouin function behavior, (see Table by Smart [41]) $\Delta Ht_m = T\Delta St_m = 1100$ J mole^{-1} °K^{-1}.

Although these values are in reasonable agreement with the idea of randomized spins above 316°K, it should be remarked, however, that the spins may be less randomized provided the value of ΔSt results from a sufficiently enhanced structural contribution compensating for a magnetic entropy decrement. The present authors thus agree with Goodenough and Kafalas [27] as to the existence of a low-spin region for MnAs above 316°K and see the high heat capacity as an indication of upper level population (*cf.* Fig. 3). Although the information that can be extracted about magnetic contributions to the heat capacity of MnAs at high temperatures is still uncertain, it apparently cannot be attributed to transitions involving a small number of levels, equal in energy for all metal atoms, but rather to a band structure occasioning less pronounced excess heat capacity.

X-Ray photographs of some MnAs samples with $x \geq 0.90$ show weak satellite lines to the strong, low-angle reflections 101, 102 and 110. These indicate the presence of a second phase in small and varying amounts. Further investigations on MnAs samples at slightly elevated temperatures in a Debye-Scherrer type camera and also on a heated diffractometer stage showed a seemingly constant intensity relationship between satellite and regular lines up to 317°K. At 317.8°K the intensity of the line adjacent to 102 had increased to 1/2 of that for 102, at 318.2°K to 2/3, at 318.7°K to 5/4, and at 319.2°K to 4/1. At 320°K the original 102 reflection had disappeared almost completely, indicating that the weak lines on the room temperature photographs were indeed caused by the presence of small amounts of the "high temperature" phase. The lines were indexed on the basis of the pseudohexagonal structure reported for this phase, and the resulting lattice constants for the coexisting phases given in Table 4.

Table 4. Lattice constants in Å for the two co-existing phases of MnAs. Only hexagonal pseudocell values are given for the orthorhombic structure (*B*31-type).

	*B*8-type		*B*31-type	
T, °K	*a*	*c*	*a*	*c*
293	3.722	5.705	3.660	5.718
315	3.721	5.704	3.662	5.706
317.8	3.720	5.705	3.660	5.708
318.7	3.714	5.712	3.659	5.710
320	—	—	3.669	5.714

The presence of two phases in varying amounts over a temperature range of more than 3°K is probably not caused by temperature gradients during the experiments, since both methods gave the same results and the gradients were presumably only a fraction of 1°K in the diffractometer set-up, where the sample was glued to a heavy copper stage and covered with aluminium foil. It is not yet known if this behavior is caused by the presence of small amounts of impurities, compositional differences between the two phases, hybrid-structure formation, or other phenomena. The absence of a uniform

transformation temperature is also reflected in the heat capacity results which remain very high, but finite, over eight consecutive runs from 315.1 to 316.6°K and a thermal equilibration period of more than 2.5 days.

The 393°K transition is apparently connected with the change in crystal structure from orthorhombic to hexagonal with increasing temperature.[22] Evaluation of the enthalpy and entropy of transition is difficult because of the large non-cooperative, Schottky-type contribution to the heat capacity of MnAs above 320°K. The Schottky-type contribution from reversions of the 3*d* electrons from the low- to the high-spin configuration amounts to 2.5 J mole^{-1}°K^{-1} at 400 °K and 2.9 J mole^{-1}° K^{-1} at 330°K. This assumption and the dilation contribution derived from Grazhdankina and Burkhanov's data [29] permit an estimate of $\Delta Ht \leq 25$ J mole^{-1} and $\Delta St \leq 0.07$ J mole^{-1} °K^{-1} for the 393°K transition.

C. Thermodynamics of formation of MnAs

Combining the entropy of MnAs given in Table 3 with the entropies of α-Mn (32.01±0.08 J mole^{-1} °K^{-1}) [42] and of metallic α-As (35.1 J mole^{-1} °K^{-1}) [43] at 298.15°K, we obtain the entropy of formation

$$\Delta Sf^\circ_{298} = 10.0 \pm 0.3 \text{ J mole}^{-1} \text{ °K}^{-1}$$

This value can be combined with enthalpy of formation data to yield the standard Gibbs energy of formation for MnAs, ΔGf°. Shchukarev, Morozova and Stolyarova[44] determined $\Delta Hf^\circ_{298} = -56.9 \pm 2.5$ kJ mole^{-1} for MnAs from the difference in heat of combustion of the compound and mixtures under identical (not specified) conditions. The manganese was reported to contain 0.7 % of impurities and the analysis gave 41.81 and 42.12 % Mn (theor. 42.31 % Mn). From these values we obtain

$$\Delta Gf^\circ_{298} = -59.9 \pm 2.5 \text{ kJ mole}^{-1} \text{ °K}^{-1}$$

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