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Thermal Study of II-IV Semiconductors: Heat Capacity and Thermodynamic Functions of Mg_2Pb from 5-300° K*

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The heat capacity of Mg_2Pb has been measured at 5–300°K, and the lattice heat capacity, Debye temperature, and thermodynamic functions have been tabulated. The following values were found for the thermodynamic functions at 298.15°K: $S^\circ_{298.15} = 72.85$ J (mole°K)$^{-1}$ and $-(G^\circ_{298.15} - H_0^\circ)/T = 59.50$ J (mole°K)$^{-1}$. The values of the experimentally determined thermodynamic functions are compared with values predicted utilizing a reduced temperature function, and are found to differ by more than experimental error.

Introduction

The Mg_2(IV) "valence compounds", Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb, are particularly intriguing because (1) they possess remarkable thermoelectric properties, (2) they have been used as model systems in which to study band structures of semiconductors, (3) the lattice dynamics of systems have the fluorite structure, and (4) they may possibly be tailored to form variable bandgap semiconductors with a bandgap adjustable within 0.78–0 eV. The last member of the series, Mg_2Pb, is from many points of view the most interesting, because there has been considerable controversy regarding the value of the bandgap in Mg_2Pb. The most recent results (*4*) indicate that Mg_2Pb is a semimetal.

The present work is the last in a series (*5*, *6*) devoted to a study of the lattice dynamics, via correlation of model calculations with heat capacity measurements, of the Mg_2(IV) compounds.

Experimental

Apparatus

Except for modifications in the sample can and for special handling of the Mg_2Pb as described below, the apparatus, a Westrum-designed adiabatic calorimeter (*7*), and experimental procedures were the same as previously described (*8*).

The new features of the can are seen in Fig. 1. A nonmetallic seal (*9*) that uses a Loctite (*10*) thread-

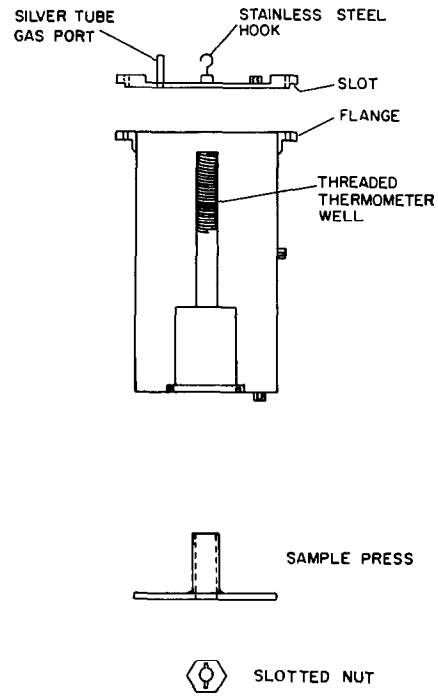

FIG. 1. Calorimeter can with Loctite seal and sample press.

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locking compound, Grade AV, was used to seal the can. As Mg_2Pb very readily reacts with water, the sample was handled in a dry box. The Loctite seal facilitated the sealing of the top and body of the can inside the dry box.

The sample can was suspended from a stainless steel hook, and thermal contact during cooling was achieved by touching the top of the container to the adiabatic shield, rather than by the use of a cone. No appreciable difference in the cooling rate was observed between this type of contact and "cone type" contacts previously used in this laboratory. Use of a hook reduced the container weight from those previously used by about 10 g.

The sample press was not threaded to fit the thermometer well as in previous containers, but rather a hexagonal brass box nut slotted to facilitate removal was used to hold the press in place. The outside of the thermometer well was threaded as before but the threads had an o.d. equal to that of the well. The container may conveniently be used for both bulk and powdered samples.

Sample Preparation

The Mg was obtained from the Dow Chemical Company and distilled in a vacuum of 10^{-9} Torr. The resistivity ratio of the distilled metal was approximately 2000. The results of a mass spectrometer analysis for minor impurities are given in Table I. The Pb was obtained from Cominco, had a stated purity of 0.999999 and has been used in this Laboratory as starting material for samples on which de Haas–van Alphen measurements were made.

TABLE I

ANALYSIS OF Mg, USED IN THE PREPARATION OF Mg_2Pb, FOR MINOR IMPURITIES[a]

Element	Impurity (atomic ppm)
O	20.0
Cl	0.1
K	0.06
Ca	0.7
Cr	2.0
Mn	0.6
Fe	1.0
Ni	15.0
Zn	1.0

[a] Analysis was made mass spectrometrically using a Nuclides Analysis Spark Source Mass Spectrograph, Nuclide Graph 2.2.

Bulk Mg_2Pb samples, roughly 6 cm long × 2 cm in diameter were grown by the Bridgeman method using an excess of 5% Mg in an attempt to insure the growth of the stoichiometric β phase of Mg_2Pb (*11*). Four such bulk samples were used for the heat capacity measurements reported in this work. The samples had the "gun blue" color characteristic of stoichiometric Mg_2Pb (*4*).

The surfaces of the bulk samples were cleaned in a dry box with an air abrasive. The samples were then crushed in a dry box with a mortar and pestle. The resulting pieces were sieved through a 2.000-mm hole size mesh and then a 0.841-mm hole size mesh to insure uniform size (*5*). The analyses for major constituents are shown in Table II. Analysis for major constituents was carried out as follows: The sample was dissolved in nitric acid. Lead was titrated with EDTA using xylenol orange as an indicator at pH 5. Magnesium did not interfere. Magnesium was determined by titrating total Mg and Pb with EDTA using erichrome black T as an indicator at pH 10, and subtracting the previously determined concentration of Pb.

To determine if there was a Mg rich Mg-Pb solid solution present as impurity, as found by Stringer and Higgins (*4*), photographs were taken at a magnification of ×500 and the results are shown in Fig. 2. The striations are grinding marks, and the shaded area in the upper center is a cavity, probably due to a chip removed during grinding. The smaller. dark areas were not initially present, but formed during the time the sample was placed under the microscope prior to shooting the photograph.

Electron microprobe analyses were also performed to determine the homogeneity of the samples used for the heat capacity measurements. The analyses were made with an A.R.L. model E.M.X.

TABLE II

MAJOR CONSTITUENT ANALYSIS RESULTS

Sample	Mg (wt %)	Pb (wt %)
1	18.76	80.80
2	18.80	80.79
3	18.82	80.81
4	19.76	80.96
5	19.85	79.81
Theoretical	19.0	81.0

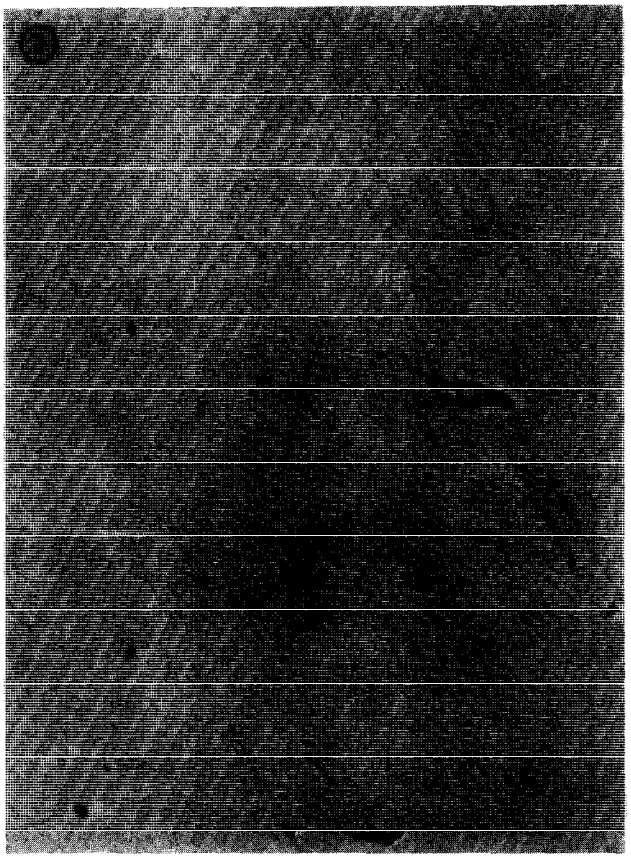

FIG. 2. Photomicrograph of Mg_2Pb used in heat capacity measurements, ×500 magnification.

microprobe. Scans were made on three representative sample particles. Each scan covered a volume 1 μ wide by 1 μ deep by 100 μ long. The scans were made on samples prepared in two different ways prior to microprobe analysis. The first scans were made on samples which had been manually polished for photomicrographs in a dry ethyl acetate-alumina slurry to prevent reaction with water. Preceding the microprobe analysis, these same samples were again polished, as aforementioned, dried, and kept in a desiccator until immediately before insertion in the microprobe vacuum system. The results of microprobe analyses on these samples were quite similar to those described by Stringer and Higgins in Fig. 4a, b of their paper (*4*). This is to say that the samples were found to be inhomogeneous. A second set of scans were made on the samples, again polished as described above, but kept under acetone until insertion in the microprobe vacuum system. These scans revealed that the samples were homogeneous to within statistical error. No points of any of these latter scans deviated from the square root of the counts at that point by more than 1.2 times the square root of the arithmetical mean of the total counts. We infer from these results that the inhomogeneities present in the dried samples were due to reaction of the surface of these samples with the atmosphere. In all probability, a hydride or a hydroxide was the contaminant seen in the microprobe analysis on the dried samples. We infer, from all analyses, that the samples were stoichiometric Mg_2Pb.

0.5653 moles of sample were loaded in the calorimeter can in a dry box and the can cover sealed with Loctite using the procedure described by Ashworth (*9*). The sample sealed in the can was then removed from the dry box, and the can was evacuated through the silver exchange gas port (See Fig. 1). Two-cm Hg pressure of He at 298°K was then introduced into the can through the silver exchange gas port and the port was sealed using standard techniques.

TABLE III

EXPERIMENTAL HEAT-CAPACITY DATA OF Mg_2Pb [J(mole°K)$^{-1}$] (0°C = 273.15°K).[a]

T_{av}(°K)	ΔT	C_p	T_{av}(°K)	ΔT	C_p
	Run 1[b]			Run 4 (cont)	
5.035	0.828	0.048	9.398	1.063	0.821
6.181	1.019	0.165	10.374	0.819	1.129
7.568	1.532	0.321	11.597	1.648	1.615
10.099	1.500	0.673	13.275	1.722	2.495
10.567	1.403	1.175	15.058	1.846	3.614
12.118	1.644	1.876	17.263	2.555	5.076
13.967	2.031	2.930	19.718	2.352	6.805
16.033	1.072	4.238			
18.179	2.217	5.726		Run 5	
20.485	2.386	7.359	21.496	2.338	8.036
22.949	2.539	9.036	24.013	2.698	9.757
25.610	2.777	10.877	26.934	3.146	11.679
28.468	2.936	12.725	29.842	2.674	13.553
31.205	2.453	14.455	32.537	2.716	15.198
33.792	2.711	15.866	35.526	3.264	17.943
40.484	4.125	19.957	39.054	3.785	19.138
45.201	5.306	22.803	43.864	5.836	21.931
50.131	4.554	25.776	49.163	4.763	24.996
54.553	4.288	28.329	53.314	3.594	27.689
58.838	4.283	30.845	56.838	3.401	29.686
	Run 2			Run 6	
49.909	3.906	25.587	49.731	3.357	15.468
58.643	4.581	30.728	52.928	3.037	27.467
63.550	5.321	33.683	56.123	3.347	29.177
68.545	4.758	36.283	60.610	5.628	31.973
73.449	5.054	38.672	65.494	4.142	34.903
78.586	5.217	41.165	70.377	5.608	37.168
88.346	4.914	46.016	75.762	5.159	39.890
94.595	7.585	47.867	80.756	4.825	42.201
102.436	8.100	50.578	85.449	4.559	44.407
110.451	7.929	52.928	90.704	5.949	46.447
118.748	8.665	55.150	97.071	6.784	48.777
128.273	10.378	57.424	104.806	8.861	51.207
138.468	10.012	59.352	113.839	8.388	53.881
158.834	10.232	61.618	123.643	10.092	56.242
169.414	10.925	64.085	134.062	10.738	58.636
			144.620	10.373	60.610
	Run 3		154.851	10.087	62.176
181.564	13.307	65.687	164.833	9.869	63.371
220.863	12.657	68.501			
233.457	12.584	69.068		Run 7	
245.853	12.238	71.829	176.140	12.548	64.868
258.065	12.220	70.597	188.085	11.355	66.090
270.544	13.561	71.432	198.872	10.253	67.127
284.181	13.775	72.422	209.051	10.125	67.945
298.195	14.492	72.963	219.121	10.022	68.554
313.173	15.338	73.699	229.084	9.930	69.418
			238.958	9.839	70.025
	Run 4		250.516	13.309	70.823
5.124	1.525	0.070	263.735	13.181	71.160
6.164	0.798	0.169	276.819	13.055	71.603
7.189	1.333	0.232	289.762	12.902	72.550
8.342	1.026	0.514	302.564	12.798	73.007

[a] At. wt of Pb = 207.21g/mole; At. wt of Mg = 24.32g/mole.

[b] A run is defined as a series of measurements. Runs are numbered chronologically.

TABLE IV

THERMODYNAMIC FUNCTIONS OF Mg_2Pb [J (mole°K)$^{-1}$] (0°C = 273.15°K)[a]

T(°K)	C_p	S_T°	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
6	0.142	0.042	0.031	0.011
10	0.949	0.260	0.203	0.057
15	3.538	1.083	0.827	0.236
20	7.001	2.574	1.957	0.627
30	13.673	6.195	4.380	1.815
40	19.702	10.959	7.461	3.498
50	25.657	16.001	10.510	5.491
60	31.563	21.201	13.527	7.674
70	37.005	26.492	16.507	9.984
80	41.880	31.754	19.377	12.377
90	46.148	36.939	22.120	14.819
100	49.793	41.995	24.710	17.285
120	55.456	51.600	29.387	22.214
140	59.696	60.485	33.430	27.055
160	62.877	68.667	36.915	31.751
180	65.282	76.217	39.939	36.279
200	67.277	83.200	42.573	40.626
220	68.695	86.679	44.884	44.795
240	69.902	95.709	46.920	48.789
260	70.989	101.348	48.730	52.618
273.15	71.660	104.865	49.818	55.048
280	71.999	106.646	50.356	56.289
298.15	72.847	111.195	51.700	59.495
300	72.932	111.645	51.831	59.815

[a] At. wt of Pb = 207.21g/mole; At. wt of Mg = 24.32g/mole.

Results

The experimental heat capacity points, uncorrected for curvature, are listed in chronological order in Table III. These points deviated from a smoothed curve by as much as 11% at 5–15°K, 1% at 15–20°K, and except for a few isolated points, less than 0.3% at 20–300°K.

The smoothed curve values of C_p and the thermodynamic functions are listed in Table IV.

The heat capacity of the addenda was 13% of the total heat capacity at 10°K, 48% at 100°K, and 49% at 300°K.

Lattice Heat Capacity

C_v and the Debye temperature θ_D, were calculated in the usual manner (*6*), using the compressibility obtained from elastic constant measurements (*12*) (2.59×10^{-12} cm^2 deg^{-1}), the coefficient of volume expansion (*13*) (3.0×10^{-5} deg^{-1}), and the molar volume (*13*) (48.085 cm^3/gfw). The calculated values of C_v and $\theta_D^{(T)}$ are listed in Table V.

Reduced Temperature Functions

As in previous work (*6*), a comparison between the present results, and those for the other Mg_2(IV) compounds is made by plotting $\theta_D(T)/\theta$ as a function of T/θ (Fig. 3). θ is the Debye temperature at 0°K as calculated from elastic constant measurements (*12*). The value of θ was taken to be 274°K.

It can be seen from Fig. 3 that θ_D/θ, the low temperature behavior of the reduced Debye temperature, is considerably different for Mg_2Pb from that for the other Mg_2(IV) compounds. This difference is reflected in the difference between the predicted (*6*) and calculated thermodynamic functions for Mg_2Pb, as shown in Table VI.

The present results yield a standard Gibbs free energy of formation at 298°K in agreement with the measured value with the value calculated by Beardmore *et al.* (*13*).

Table VII compares $\Delta G_f^0(0)$ and $\Delta G(0)$ of this work with the previously predicted values.

TABLE V

C_v [J (mole°K)$^{-1}$] AND THE DEBYE TEMPERATURE PER ATOM FOR Mg_2Pb, SMOOTHED CURVE VALUES

T(°K)	C_v	θ_D(°K)
5	0.0723	216.0
6	0.1416	107.6
7	0.2530	199.5
8	0.4180	192.8
9	0.6465	187.4
10	0.9496	185.2
15	3.5374	176.7
20	7.001	185.4
25	10.442	199.3
30	13.671	213.9
35	16.710	228.9
40	19.697	241.2
45	22.675	252.0
50	25.647	261.0
60	31.544	274.8
70	36.975	284.2
80	41.836	292.0
90	46.088	295.2
100	49.715	298.0
120	55.340	304.8
140	59.539	307.1
160	62.678	307.2
180	65.041	306.2
200	66.943	302.6
220	68.369	299.0
240	69.534	292.8
260	70.578	283.4
280	71.534	268.0
300	72.431	244.0

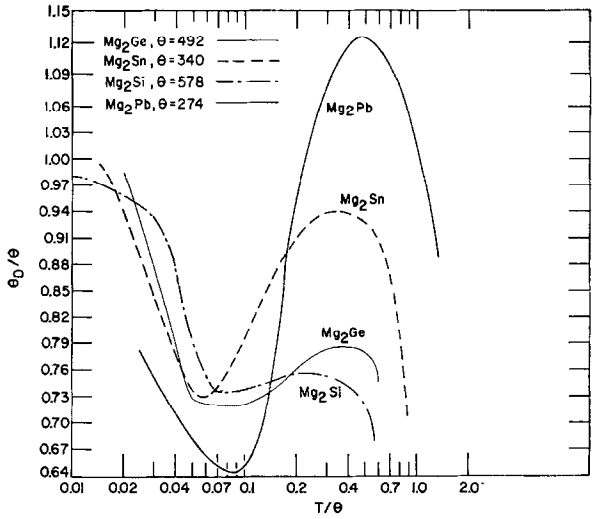

FIG. 3. Reduced Debye temperature as a function of reduced temperature for the Mg_2(IV) compounds.

Discussion

The present heat capacity measurements yield thermodynamic functions for Mg_2Pb which do not appreciably alter the conclusions previously made regarding the trends in the Mg_2X series. It has been suggested, in view of the results of elastic constant measurements, that the series should be considered in two groups, the first being Mg_2Si–Mg_2Ge and the second Mg_2Sn–Mg_2Pb (*12*). The present results are not in disagreement with this idea, as illustrated by Fig. 4, in which the standard Gibbs free energy change for the reaction $2Mg(s) + X(g) = Mg_2X(s)$ at 0°K is plotted as a function of the

TABLE VI

TABULAR CALCULATION FOR ΔG_f° (298) FOR Mg_2Pb

ΔH_f[273][kJ(gfw)$^{-1}$]	$S^\circ_{(298)}$[J(gfw·deg)$^{-1}$]	$S^\circ_{(298)}$[J(gfw·deg)$^{-1}$] (elemental sum)	$\Delta S^\circ_{(298)}$[J(gfw)$^{-1}$]
−49.8[a]	118.94[b] 111.16[c]	129.83	−10.89[b] −18.67[c]
C_p(298)[J(gfw·deg)$^{-1}$]	C_p(298)[J(gfw·deg)$^{-1}$] (elemental sum)		ΔC_p(298)[J(gfw·deg)$^{-1}$]
74.41[b] 72.84[c]	74.52		−0.11[b] −1.68[c]
	ΔH_f°(298)[kJ(gfw)$^{-1}$]		ΔG_f°(298)[kJ(gfw)$^{-1}$]
	−49.8[b] −49.8[c]		−46.6[b] −44.2[c] −42.7 ± 2.5[a]

[a] Beardmore, *et al.* (*13*). [b] Gerstein, *et al.* (*6*). [c] This work.

TABLE VII

$\Delta G_f^\circ(O)$, $\Delta G(O)$, $\Delta H^\circ(O)$ IN kJ(gfw)$^{-1}$.

$\Delta G(O)$ $2Mg(s,0) + Pb(s,0) = Mg_2Pb(s,0)$	$\Delta G(O)$ $2Mg(s,0) + Pb(g,0) = Mg_2Pb(s,0)$	$\Delta H_0(O)$ $Pb(g,0) = Pb(s,0)$
−50.2[a]	−246.7[a]	−196.48[b]
−49.7[c]	−246.2[c]	

[a] B. C. Gerstein, *et al.*, *J. Chem. Phys.* **47**, 2109 (1967).
[b] G. N. Lewis and M. Randall, "Thermodynamics", 2nd Ed. New York, 1971.
[c] This work.

Slater radius (*15*) of X. The reason for this behavior could well be the increased *d* band participation to binding and conduction in Sn and, by inference, Pb, as inferred from both the Engel–Brewer correlation (*16*) and from the work of Phillips (*17*).

Phillips' dielectric scale of electronegativity (*17, 18*) offers the tantalizing possibility of utilizing the dielectric electronegatives of Pb and Mg in the Mg_2X series via standard heats of formation. Unfortunately, the co-ordination numbers of Mg and X in Mg_2X are neither four nor six, and the present authors have not been creative enough to relate dielectric electronegativities to standard heats of formation for the Mg_2X series. Hopefully, this work will stimulate thinking along these lines for future workers.

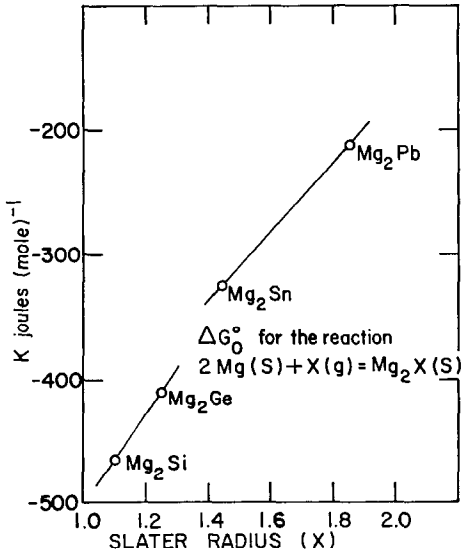

FIG. 4. Standard heat of formation at 0°K for the $Mg_2(IV)$ compounds as a function of Slater radius of X.

Summary

The heat capacity of Mg_2Pb has been measured and thermodynamic functions have been calculated at 5–300°K. The experimental heat capacity at 298°K was found to be 2.2% less than a value predicted using a corresponding states scheme. The Gibbs free energies of formation at 298°K and 0°K have been found to agree with an extrapolation made in earlier work to within 5% at 298°K and 1% at 0°K.

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References

1. M. W. Heller and G. C. Danielson, *J. Phys. Chem. Solids* **23**, 601 (1962).
2. P. M. Lee, *Phys. Rev.* **135**, A110 (1965); N. O. Folland, *Phys. Rev.* **158**, 764 (1967;) M. Y. Anyang and M. L. Cohen, *Solid State Comm.* **6**, 855 (1968).
3. P. L. Chung, W. B. Whitten, and G. C. Danielson, *J. Phys. Chem. Solids* **26**, 49 (1965); P. L. Chung, W. B. Whitten, and G. C. Danielson, *J. Phys. Chem. Solids* **26**, 1755 (1965).
4. G. A. Stringer and R. J. Higgens, *J. Appl. Phys.* **41**, 489 (1970).
5. B. C. Gerstein, P. L. Chung, and G. C. Danielson, *J. Phys. Chem. Solids* **27**, 1161 (1966); F. J. Jelinek, W. D. Schickell, and B. C. Gerstein, *J. Phys. Chem. Solids* **28**, 267 (1967).
6. B. C. Gerstein, *et al.*, *J. Chem. Phys.* **47**, 2109 (1967).
7. E. F. Westrum, Jr., *Advan. Cryog. Eng.* **7**, 1 (1962).
8. B. C. Gerstein, W. A. Taylor, W. D. Schickell, and F. H. Spedding, *J. Chem. Phys.* **51**, 2924 (1969).

9. T. ASHWORTH AND H. STEEPLE, *Cryogenics* **7**, 225 (1968).
10. Loctite is a commercial thread-locking compound made by the Loctite Corporation.
11. J. M. ELRIDGE, E. MILLER, AND K. L. KOMAREK, *Trans. AIME* **233**, 1303 (1965).
12. P. L. CHUNG AND G. C. DANIELSON, USAEC Report IS-1451, (1966).
13. This value was obtained by extrapolation of the Mg_2Si, Mg_2Ge and Mg_2Sn data.
14. P. BEARDMORE, B. W. HOWLETT, B. D. LICHTER, AND M. B. BEVER, *Trans. AIME* **236**, 102 (1966).
15. J. C. SLATER, *J. Chem. Phys.* **41**, 3199 (1964).
16. L. BREWER, "Electronic Structure and Alloy Chemistry", (Paul A. Beck, Ed.), pp. 221, Interscience, New York, 1963.
17. J. C. PHILLIPS, *Phys. Rev. Lett.* **20**, 550 (1968).
18. J. C. PHILLIPS, *Phys. Rev. Letters* **19**, 415 (1967); *Phys. Rev. Lett.* **22**, 645 (1969); *Phys. Today* **23**, 23 (1970).