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A measurement of the heat capacity of CaMg_2 and a calculation of the cohesive energy of CaMg_2

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AND A CALCULATION OF THE COHESIVE ENERGY OF
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A MEASUREMENT OF THE HEAT CAPACITY OF CaMg_2
AND A CALCULATION OF THE COHESIVE ENERGY OF CaMg_2

by

Joseph Edward Davison

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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Approved:

Signature was redacted for privacy.

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1966

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INTRODUCTION

One of the relevant areas of interest in the field of metallurgy is the study of phase stability of solids. The quantitative basis for such studies is provided by the thermodynamic functions. The criterion for the thermodynamic stability of a phase is that the free energy of formation of the phase from its constituents be negative. An evaluation of the free energy of formation, ΔF_f , can be accomplished by determining the enthalpy of formation, ΔH_f , and the entropy of formation, ΔS_f , and relating these quantities to the free energy by the expression,

$$\Delta F_f = \Delta H_f - T\Delta S_f .$$

A method of measuring the entropy of formation is suggested by the Third Law of Thermodynamics. This Law states that the value of the entropy of a crystalline solid in complete internal equilibrium is zero at the absolute zero of temperature. The entropy of CaMg_2 was evaluated from the heat capacity measurements. These data were combined with the existing entropy information of the elements to yield the entropy of formation of the compound. The heat capacity was measured below room temperature in an adiabatic calorimeter. Above room temperature, the heat capacity was extracted from

measurements of the heat content, which was measured relative to the value at 273.1°K with the aid of an ice calorimeter.

The heat capacity measurements also provide the necessary information to evaluate the temperature dependence of the enthalpy of formation. These heat capacity data were combined with existing information to obtain the value of the enthalpy of formation at 0°K.

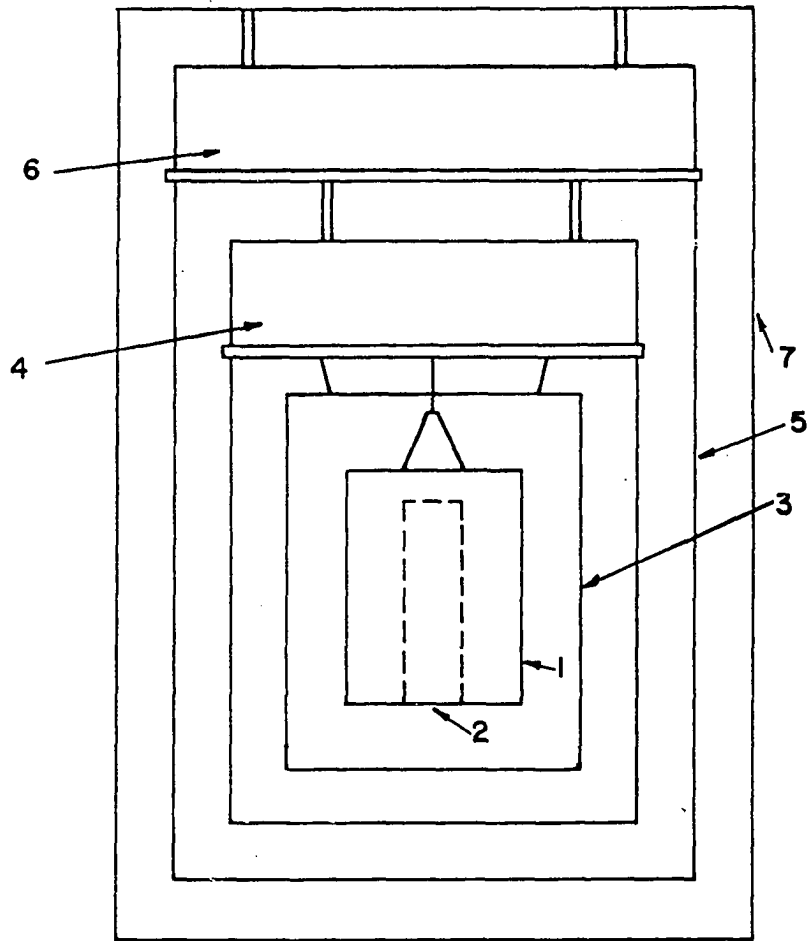
The enthalpy of formation of the intermetallic compound, CaMg_2 was approximated as the difference between the cohesive energies of the compound and of the elemental constituents. The cohesive energies were obtained from a modification of the Wigner-Seitz approach. This approach has been reasonably successful in quantitative calculations of the enthalpy of sublimation of the elements. The calculations of the enthalpy of formation were extended to the intermediate phases, SrMg_2 and BaMg_2 . The results of these calculations show qualitative agreement between the measured and calculated values.

MEASUREMENT OF THE HEAT CAPACITY OF CaMg_2 FROM 4.87°K TO 286.64°K

The heat capacity of CaMg_2 was measured over the temperature interval of 4.87°K to 286.64°K in an adiabatic calorimeter. The procedure for measuring the heat capacity consists of transferring a measured amount of heat energy to the sample and measuring the associated temperature rise. The mean heat capacity, \bar{C} , may be expressed by the relation,

$$\bar{C} = \frac{\Delta E}{\Delta T} . \quad (1)$$

where ΔE is the amount of energy delivered to the sample and ΔT is the temperature rise of the sample. The physical details of the calorimeter and the experimental procedure for the measurements have been described by Gerstein et al. (1966). The design of the calorimeter is illustrated in Figure 1. The CaMg_2 powder was sealed in the sample container, 1, and the sample container was suspended inside of a thermal shield, 3, that was maintained at the same temperature as the sample. Surrounding this shield was another shield, 4, which was maintained at liquid nitrogen temperature. The entire assembly was suspended inside of an evacuated chamber, 7. Temperature differences between the shield, 3, and the sample



1. SAMPLE CONTAINER
2. THERMOMETER AND HEATER WELL
3. ADIABATIC SHIELD
4. LIQUID HELIUM RESERVOIR
5. SHIELD MAINTAINED AT 77°K
6. LIQUID NITROGEN RESERVOIR
7. EVACUATED CONTAINER

Figure 1. An illustration of the adiabatic calorimeter in which the heat capacity of CaMg_2 was measured

container, 1, were sensed by three separate thermocouple circuits and when required an electrical heater which was wound around the shield was energized in order to maintain the shield at the same temperature as the sample.

Heat energy was supplied to the sample by dissipating electrical energy in a manganin resistance heater. This heater together with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards was inserted in a well, 2, which was located in the bottom of the sample container.

Since adiabatic conditions were difficult to achieve an experimental procedure was followed which compensated for the heat leaks. This procedure consisted of measuring the time rate of change of the temperature of the sample before and after heat inputs. The temperature of the sample before and after the heat inputs was extrapolated to the center of the heating period. These extrapolations were based on the best fit of a straight line through the measured time rate of change of the temperature. The difference at the center of the heating period between the extrapolated lines was taken as the measure of the temperature rise due to the heat input. The electrical energy, ΔE , supplied to the heater was deter-

mined by measuring the potential drop, V_N , across the heater, the potential drop, V_R , across the standard resistance, R , which was in series with the heater, and the time, t , that the heater was energized. The relation among these quantities is expressed by the following equation,

$$\Delta E = t V_N V_R / R. \quad (2)$$

The mean heat capacity was then calculated from Equation 1. In order to compensate for the heat capacity of the sample container, the heater, and the thermometer, measurements of the heat capacity over the entire temperature interval were carried out with and without the sample in place. The difference between these two sets of measurements is the heat capacity of the sample.

The calcium and the magnesium were purified by vapor distillation at the Ames Laboratory. Chemical analyses of the calcium and magnesium are listed in Table 1. A mixture of the elements was sealed in a tantalum container under an argon atmosphere. This mixture was heated to 900°C and maintained at that temperature for four hours. The alloy was cooled to room temperature and subsequently mechanically pulverized. The powdered material was annealed at 400°C for two weeks in a sealed container under an argon atmosphere to

insure a homogeneous alloy. The presence of the CaMg_2 phase was verified by an analysis of x-ray powder photographs and all of the observed lines were accounted for by the CaMg_2 phase. The results of a chemical analysis of the alloy are listed in Table 2. According to the phase diagram recorded by Hansen (1958), alloys of this composition are in the two phase region which consists of α -calcium and CaMg_2 . The observed heat capacities were corrected for the presence of the α -calcium phase with the α -calcium heat capacity values tabulated by Hultgren et al. (1963). The corrected heat capacities for CaMg_2 are tabulated as a function of temperature in Table 3. The free energy function and the absolute entropy of CaMg_2 , which were calculated from the experimental heat capacity data, are listed in Table 4.

A smooth curve was fitted to a plot of the experimental values of the heat capacity and in only two instances above 30°K did the plotted points deviate from the curve by more than 0.2 percent. Below 10°K the deviation of several of the points was as much as 50%. These large percentage deviations were attributed to the small value of the heat capacity and to the low sensitivity of the platinum resistance thermometer in this temperature range. The deviations in the region of

10°K to 30°K were less than five percent. Although the percentage deviations of some of the low temperature measurements is large, the actual value of these deviations is small since the magnitude of the heat capacity in that temperature range is small. On the basis of these deviations the error in the value of the third law entropy at 298.15°K was estimated to be less than 0.01 cal/K°/gm.-atom.

A value of $-0.25 \pm .06$ cal/gm.-atom/K° was obtained for the standard entropy of formation at 298.1°K from the relation,

$$\Delta S_F^\circ = S_{\text{CaMg}_2}^\circ - 2/3 S_{\text{Mg}}^\circ - 1/3 S_{\text{Ca}}^\circ.$$

The values of S_{Mg}° and S_{Ca}° at 298.1°K were taken from the compilation of Hultgren et al. (1963).

Table 1. Chemical analyses of calcium and magnesium

Calcium		Magnesium	
Element	Content	Element	Content
Ca	~99.90%	Mg	~99.95%
C	200 ppm	C	250 ppm
Mg	50 ppm	N	45 ppm
N	50 ppm	Fe	40 ppm
O	100 ppm		

Table 2. Chemical analysis of the specimen used in the low temperature heat capacity measurement

Element	Analyzed weight percent
Ca	46.68
Mg	53.02

Table 3. Heat capacity of CaMg_2 (C_p) cal/gm. at./ K°

Temp. $^\circ K$	C_p	Temp. $^\circ K$	C_p
		69.56	2.799
4.87	0.0102	69.95	2.817
5.18	0.0071	75.48	3.086
5.25	0.0009	76.50	3.131
5.64	0.0020	81.43	3.355
6.10	0.0035	84.33	3.478
6.57	0.0043	89.88	3.685
7.46	0.0052	94.29	3.834
7.79	0.0063	99.58	4.000
8.94	0.0119	110.01	4.284
9.30	0.0125	115.99	4.430
9.88	0.0191	120.37	4.534
10.90	0.0186	126.32	4.656
11.09	0.0166	129.70	4.720
12.46	0.0200	135.86	4.829
12.91	0.0258	138.49	4.870
14.37	0.0358	145.26	4.980
14.93	0.0383	148.69	5.029
16.43	0.0548	155.12	5.117
17.24	0.0674	159.81	5.182
18.90	0.0909	165.40	5.241
19.83	0.1102	170.85	5.261
21.61	0.1537	176.02	5.348
22.82	0.1859	181.90	5.402
24.45	0.2365	189.23	5.466
26.11	0.2986	193.07	5.502
27.12	0.3309	198.32	5.548
29.73	0.4520	203.15	5.581
29.77	0.4580	208.61	5.610
33.06	0.6177	213.20	5.638
33.73	0.6764	219.69	5.678
37.18	0.8574	224.48	5.720
38.16	0.9170	231.35	5.749
41.89	1.147	236.31	5.579
43.09	1.223	243.33	5.813
46.96	1.469	248.51	5.832
48.63	1.577	255.31	5.873
51.48	1.760	260.96	5.885
52.71	1.832	267.49	5.917
57.53	2.127	273.71	5.927
63.21	2.402	280.08	5.950
63.76	2.494	286.64	5.995

Table 4. Thermodynamic functions of CaMg_2 in cal/deg. $\dot{\text{K}}/\text{gm-atom}$

$T^\circ\text{K}$	$(F^\circ - H_0^\circ)/T$	S°
10.0	-0.004	0.005
20.0	-0.011	0.038
30.0	-0.036	0.153
40.0	-0.088	0.358
50.0	-0.169	0.646
60.0	-0.277	0.997
70.0	-0.408	1.389
80.0	-0.556	1.801
90.0	-0.718	2.219
100.0	-0.889	2.630
110.0	-1.065	3.027
120.0	-1.244	3.408
130.0	-1.424	3.774
140.0	-1.604	4.125
150.0	-1.784	4.463
160.0	-1.961	4.792
170.0	-2.138	5.111
180.0	-2.312	5.420
190.0	-2.484	5.718
200.0	-2.653	6.005
210.0	-2.819	6.278
220.0	-2.982	6.538
230.0	-3.142	6.786
240.0	-3.298	7.027
250.0	-3.452	7.263
260.0	-3.604	7.498
270.0	-3.753	7.731
280.0	-3.899	7.948
290.0	-4.038	8.119
298.15	-4.146	8.272

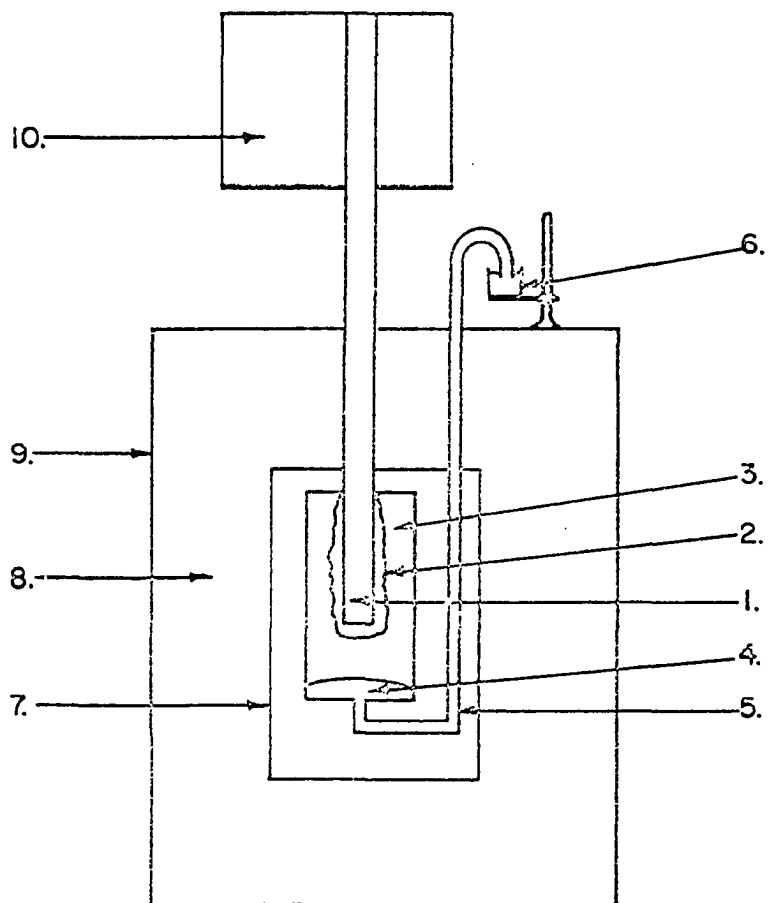
THE HEAT CONTENT OF CaMg_2 FROM 273°K TO 673°K

The heat content relative to 0°C of a 1.8064 gram sample of a calcium-magnesium alloy was measured between 0°C and 400°C . The starting materials and the sample preparation were identical to that described in the previous section.

Since a detailed description of the apparatus and of the experimental procedure has been presented by Spedding et al. (1960), only a brief description will be given here. The principal parts of the apparatus are illustrated in Figure 2. The experimental procedure consists of dropping the sample, which has been allowed to reach thermal equilibrium within a furnace cavity, into the inner chamber of an ice calorimeter and measuring the amount of heat energy transferred to the calorimeter. The heat energy causes some of the ice to melt and the volume contraction associated with this phase transformation causes a proportionate amount of mercury to be drawn into the ice calorimeter from the mercury reservoir. Thus the weight loss in the mercury reservoir can be directly related to the heat transferred from the sample.

The enthalpy at temperature, T , relative to 273°K may be expressed by the relation,

$$H_T - H_{273} = Q/n, \quad (3)$$



1. SAMPLE CHAMBER
2. ICE MANTLE
3. DISTILLED WATER
4. MERCURY
5. CAPILLARY TUBE
6. MERCURY RESERVOIR
7. EVACUATED CONTAINER
8. CONSTANT TEMPERATURE ICE BATH
9. INSULATED CONTAINER
10. FURNACE

Figure 2. An illustration of the equipment in which the heat content of CaMg_2 was measured

where Q is the heat energy measured and n is the number of moles of the substance.

Heat leaks into and out of the ice calorimeter were minimized by immersing it in an ice bath. Even with this precaution slight heat leaks were still observed. Their effect on the experiment was compensated by measuring the heat leaks before and after each drop and applying these corrections to the data.

The calcium-magnesium sample was sealed together with an argon atmosphere in a tantalum container, which in turn was sealed in a platinum container. The heat content of the sample was obtained as the difference between the measurements on an empty container and a container with the sample. This method has the added advantage of minimizing systematic errors due to the experimental procedure.

The results of a chemical analysis of the sample are listed in Table 5. These results indicate that the sample is in the two phase region consisting of magnesium and CaMg_2 . The observed heat content values were corrected for the magnesium phase present in the sample with the enthalpy values of magnesium listed by Hultgren et al. (1963). The corrected values of the enthalpy of CaMg_2 are listed in Table 6.

The enthalpy difference, $H_T - H_{298.1}$, was evaluated from a polynomial of degree two which had been fitted to the experimental data by the method of least squares. The deviations of the experimental points from the fitted curves are listed in Table 6. Table 7 lists the enthalpy values calculated from the fitted curve.

The entropy difference, $S_T - S_{298.1}$, was evaluated by a method suggested by Hultgren et al. (1963). Following their suggestions the mean heat capacity of each enthalpy datum point was calculated and the mean heat capacity data were fitted to a straight line by the method of least squares. The measured values of the low temperature heat capacity and the mean heat capacity values calculated from the heat content data are shown in Figure 3. The discontinuity at 273°K between the straight line fit and the values from the adiabatic heat capacity measurements is less than 0.5 percent. The entropy difference was calculated with the aid of the fitted line from the relation,

$$S_T - S_{298.1} = \int_{298.1}^T \frac{\bar{C}_p}{T} dT \quad (4)$$

These values are tabulated in Table 7. Values above 470°K were calculated from an extrapolation of the fitted \bar{C}_p curve.

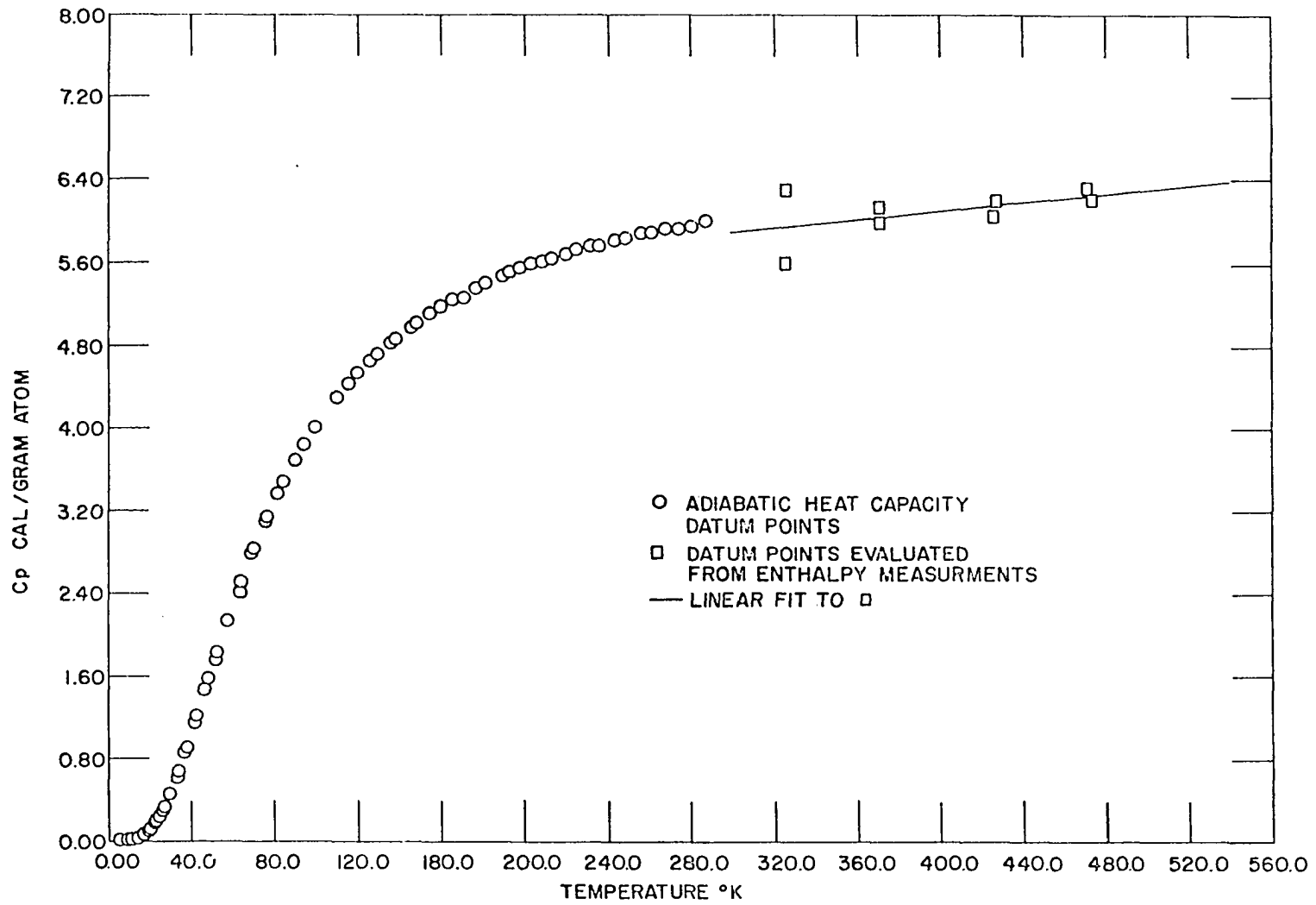


Figure 3. Heat capacity of CaMg₂

Table 5. Chemical analysis of the specimen used in the enthalpy measurements over the temperature interval 0°C to 400°C

Element	Weight
Ca	43.25
Mg	55.97

Table 6. The values of the enthalpy of CaMg₂ measured relative to the value at 273.1°K

T °K	H _T -H _{273.1} cal/gm-at	Deviation from fitted curve cal/gm-at.	$\frac{H_T - H_{273.1}}{T - 273.1}$ cal/gm-at/K. deg
376.8	580.2	37.20	5.595
377.2	655.6	-35.78	6.298
464.8	1158.7	-00.50	6.044
465.2	1176.4	15.70	6.124
578.0	1847.4	30.55	6.061
582.2	1913.1	- 7.93	6.191
669.6	2511.7	-31.52	6.335
674.6	2492.1	21.46	6.207

Table 7. The enthalpy and entropy relative to their values at 298.1°K

Temp. °K	$H_T - H_{298.1}$ cal/gm-atom	$S_T - S_{298.1}$ cal/gm-atom/K°
300	10.9	0.037
310	69.9	0.231
320	129.1	0.419
330	188.6	0.603
340	248.2	0.781
350	308.0	0.955
360	368.1	1.125
370	428.4	1.290
380	488.9	1.452
390	549.6	1.610
400	610.5	1.764
410	671.6	1.915
420	732.9	2.063
430	794.5	2.208
440	856.2	2.350
450	918.2	2.490
460	980.4	2.626
470	1042.8	2.760
480	1105.4	2.892
490	1168.2	3.022
500	1231.2	3.149
510	1294.4	3.274
520	1357.9	3.397
530	1421.5	3.518
540	1485.4	3.638
550	1549.5	3.755
560	1613.8	3.871
570	1678.3	3.985
580	1743.0	4.097
590	1807.9	4.208
600	1873.1	4.317
610	1938.4	4.425
620	2004.0	4.531
630	2069.7	4.636
640	2135.7	4.740
650	2201.9	4.842
660	2268.3	4.943
670	2334.9	5.043
680	2401.8	5.141
690	2468.8	5.239
700	2536.1	5.335

THE COHESIVE ENERGY

The cohesive energy of an elemental metal is defined as the energy required to separate an equilibrium solid phase into free neutral atoms at 0°K . For those elements which vaporize as a monatomic species, the experimental measure of the cohesive energy is the enthalpy of sublimation extrapolated to the absolute zero of temperature.

A calculation of the cohesive energy consists of:

- 1.) Formulating a Hamiltonian operator which, together with the correct wave function, describes the energy states of the substance,
- 2.) solving the resulting differential equation with the appropriate boundary conditions on the wave functions, and
- 3.) comparing the average energy of the electrons of the solid to their energy in the free atoms. The difference between these two energies of these two states is the cohesive energy of the solid.

If the magnetic interactions are neglected, and if the zero point vibrations of the nuclei are neglected, then the Hamiltonian operator for a system of N nuclei and zN electrons may be written as,

$$\begin{aligned}
H_{\text{op}} = & - \sum_{i=1}^{Z_n} \frac{2}{\partial_m} \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^N \sum_{j=1}^{Z_n} \frac{Z_i e^2}{R_i - r_j} + \frac{1}{2} \sum_{i \neq j}^{Z_n} \sum_{j=1}^{Z_n} \frac{e^2}{r_i - r_j} \\
& + \frac{1}{2} \sum_{i \neq j}^N \sum_{j=1}^N \frac{Z_i Z_j e^2}{R_i - R_j} \tag{5}
\end{aligned}$$

where Z_i is the number of electronic charges on the i^{th} nucleus, r_i is the position vector of the i^{th} electron, and R_j is the position vector of the j^{th} nucleus. With the introduction of the appropriate wave function, the physical sense of the summations of this equation are, in the order of their appearance: 1) the kinetic energy of all the electrons, 2) the potential energy due to the coulomb attraction between the nuclei and the electrons, 3) the potential energy due to the coulomb repulsion amongst all the electrons, and 4) the potential energy due to the coulomb interactions of all the nuclei. An exact solution to this differential equation would yield the cohesive energy, the crystal structure, the equilibrium lattice spacing, the elastic constants, and the electronic charge distribution. Unfortunately, exact solutions for this problem have not yet been formulated.

Wigner and Seitz (1933) suggested an approach to the

calculation of cohesive energies of elemental alkali metals. Their method consists of dividing the crystal into cells which completely fill the crystal volume. The Wigner-Seitz cell is defined in the case of the elements in the following manner. The interatomic vectors between an atom and its nearest and next nearest neighbors are bisected by planes which are normal to the respective interatomic vectors. The smallest volume enclosed by these planes and containing the reference atom is defined as the Wigner-Seitz cell. Each cell contains a positively charged ion and a number of valence electrons sufficient to maintain electrical neutrality. The boundary conditions imposed on the ground state wave function are: 1.) that the wave function have the same periodicity as the lattice, and 2.) that the value of the normal derivative be zero at the cell boundary. A further approximation is made by replacing the original cell by a sphere of equal volume. The boundary conditions are modified so that the value of the normal derivative of the ground state wave function be zero at the surface of the sphere. Since the cells are assumed to be electrically neutral and since they are a close approximation to a sphere, the interactions amongst the cells are neglected. Thus, the problem

for elemental substances consists of calculating the energy of the valence electrons in one cell.

Raimes (1952) has carried out cohesive energy calculations for a number of divalent metals. His expression for the energy of the valence electrons as a function of the radius of the sphere consists of five terms,

$$E(R_s) = Z \left(\frac{R_0^2}{R_s^3} - \frac{3}{R_s} \right) + \frac{1.2Z}{R_s} + \frac{2.21Z^{2/3}}{R_s^L} + \frac{0.916Z^{1/3}}{R_s} + (0.031 \ln(R_s Z^{-1/3}) - .115) \quad (6)$$

The first term on the right represents the ground state energy of the valence electrons. The R_s represents the radius of the Wigner-Seitz sphere and the R_0 represents the radius of that sphere corresponding to the minimum value of the ground state energy term. The next three terms of (6) are the Coulomb self energy, the Fermi energy, and the exchange energy. These terms are evaluated by assuming that the electrons in the higher states behave as a free electron gas. The final term in (6) represents the correlation energy. This particular expression of the correlation energy is due to Pines (1955). Raimes (1963) suggests that this expression for the correlation energy should be valid in the region of metallic densities.

Brooks (1963) has calculated the cohesive energy of elements in Groups III and IV of the Periodic Chart. His calculations are similar to those of Wigner and Seitz (1933) and of Raimes (1952) in that he has calculated a ground state energy for the conduction electrons and treated the higher energy states by the free electron approximation with corrections for coulomb, exchange, and correlation energies of the electron gas.

In the present work an attempt has been made to extend this approach to binary alloys. In this extension the ground state energy of the valence band in an alloy was approximated by the arithmetic mean of the ground state energies of the elemental constituents, i.e.,

$$E_0 = N_1 E_{01} + N_2 E_{02}, \quad (7)$$

where E_0 is the ground state energy of the alloy E_{01} and E_{02} are the ground state energies of the respective elements, and N_1 and N_2 are the mole fractions of the respective elements.

In order to evaluate the E_0 of Equation 7, atomic polyhedra were defined for the atoms of the alloy in a manner similar to the definition of the Wigner-Seitz cell. Planes are constructed normal to the interatomic vectors between a reference atom and its nearest and next nearest neighbors.

The atomic polyhedron is defined as the smallest volume enclosed by this set of planes and containing the reference atom, and each polyhedron is subsequently replaced by a sphere of equal volume.

In the elemental case, the ground state energy term is related to the radius of the Wigner-Seitz sphere by the expression,

$$E_0 = Z \left(\frac{R_0^2}{R^3} - \frac{3}{R} \right) \quad (8)$$

For the case of an alloy, the terms E_{01} and E_{02} were assumed to be related to radii, R_1 and R_2 , of their respective Wigner-Seitz spheres in the alloy by the expressions;

$$E_{01} = Z \left(\frac{R_{01}^2}{R_1^3} - \frac{3}{R_1} \right) \quad (9)$$

$$E_{02} = Z \left(\frac{R_{02}^2}{R_2^3} - \frac{3}{R_2} \right) \quad (10)$$

The values of R_{01} and R_{02} were assumed to be the same in the alloy as in the elemental case.

The occupied states of higher energy were calculated on the assumption that the electrons behaved as free electrons with the corrections to the energy for Coulomb, exchange, and correlation interactions. The average energy per electron of the higher states which is denoted by E_{HS} was calculated from

the relation,

$$E_{12}(\tau) = \frac{2.21Z^{2/3}}{R^2} + \frac{2.14Z}{R} - \frac{.513Z^{2/3}}{R} + (.031 \ln (R Z^{-1/3}) - .115) \quad (11)$$

where R is defined by the relation,

$$R^3 = n_1 R_1^3 + n_2 R_2^3, \quad (12)$$

and is a measure of the volume of the alloy.

The average energy per electron of an alloy was found by summing the ground state term, (7), with the energy expression for the higher occupied states, (11). With the appropriate substitution for E_{01} and E_{02} , the expression for the average energy is,

$$E = n_1 \left[\frac{2.21Z^{2/3}}{R_1^2} - \frac{.513Z^{2/3}}{R_1} + \frac{2.14Z}{R_1} + (.031 \ln (R_1 Z^{-1/3}) - .115) \right] + n_2 \left[\frac{2.21Z^{2/3}}{R_2^2} - \frac{.513Z^{2/3}}{R_2} + \frac{2.14Z}{R_2} + (.031 \ln (R_2 Z^{-1/3}) - .115) \right]. \quad (13)$$

In contrast to the cohesive energy relation of a given element, (3), which is a function only of the size of the Wigner-Seitz cell, the cohesive energy expression for an alloy, (13) contains two adjustable parameters, the ratio of R_2 to R_1 and the quantity, τ , which is defined in (11).

The quantities of interest that can be calculated with the aid of Equation 13 are,

- 1.) The enthalpy of formation,
- 2.) the volume of the alloy, and
- 3.) the bulk modulus.

The enthalpy of formation was approximated by the difference between the cohesive energy of the compound and the sum of the cohesive energy of the elements. Thus the enthalpy of formation may be calculated as a function of the cell size of the compound from the relation,

$$\Delta H_f \cong E - N_1 E_1 - N_2 E_2, \quad (14)$$

where E_1 and E_2 are the cohesive energies of the respective elements. This approximation neglects the differences between the zero point energies of the respective materials.

The volume of an alloy was calculated from the relation,

$$V = \frac{4}{3} \pi R^3, \quad (15)$$

where R is the quantity defined in Equation 12. The equilibrium volume is that volume which corresponds to the minimum in the cohesive energy versus volume relation. Finally, the bulk modulus was obtained from the relation,

$$B = \frac{1}{12\pi R_{eq}} \left. \frac{\partial^2 E}{\partial R^2} \right|_{R_{eq}} \quad (16)$$

DISCUSSION

The standard enthalpy of formation was obtained at the absolute zero of temperature from the relation,

$$\Delta H_{\text{O}}^{\circ} = \Delta H_{\text{T}}^{\circ} - \int_{\text{O}}^{\text{T}} C_{\text{PCaMg}_2} dT + \int_{\text{O}}^{\text{T}} \left(\frac{2}{3} C_{\text{PMg}} + \frac{1}{3} C_{\text{PCa}} \right) dT$$

The first integral was evaluated from the experimental heat capacity and heat content data presented above, while the last integral was evaluated from the data compiled by Hultgren et al. (1963). The existing data for the heat of formation of CaMg_2 are listed in Table 8. The lack of any appreciable temperature dependence of the enthalpy of formation is in agreement with the Kopp-Neuman Rule which states that the heat capacity of a metallic alloy may be approximated by the sum of the heat capacities of the constituent elements.

The equilibrium volumes of the elements and of the compound were calculated from the lattice parameters tabulated by Pearson (1958). A volume contraction of 5.66% was found from these data to be associated with the formation of the compound CaMg_2 .

The validity of the cohesive energy expression of an alloy, (13), was assessed by comparing the experimental and calculated values of the enthalpy of formation and the

volume contraction. The calculated values of the enthalpy of formation and the equilibrium volume were obtained from relations (10) and (11). The quantity, ΔH_f , given by Equation 10 is, by virtue of its relation to the cohesive energy, a function of the same two adjustable parameters, R and the ratio of R_2 to R_1 . The procedure for calculating the enthalpy of formation consisted in calculating the cohesive energy as a function of R with the ratio of R_2 to R_1 held constant. The values of the R_0 's required for the evaluation of (10) were obtained from the treatment of the divalent metals by Raimes (1952). A representative plot of the cohesive energy calculation as a function of R with the size ratio held constant at $R_2/R_1 = \sqrt{1.5}$ is shown in Figure 4. The point corresponding to the calculated values of the energy minimum and the equilibrium volumes of the equivalent constituents is also indicated. The difference between this point and the minimum point of the curve are measures of the enthalpy of formation and the volume change associated with compound formation. This difference is on the order of one per cent of the value calculated for the cohesive energy of the compound.

The values of the enthalpy of formation, and the volume change associated with formation of the alloy were then

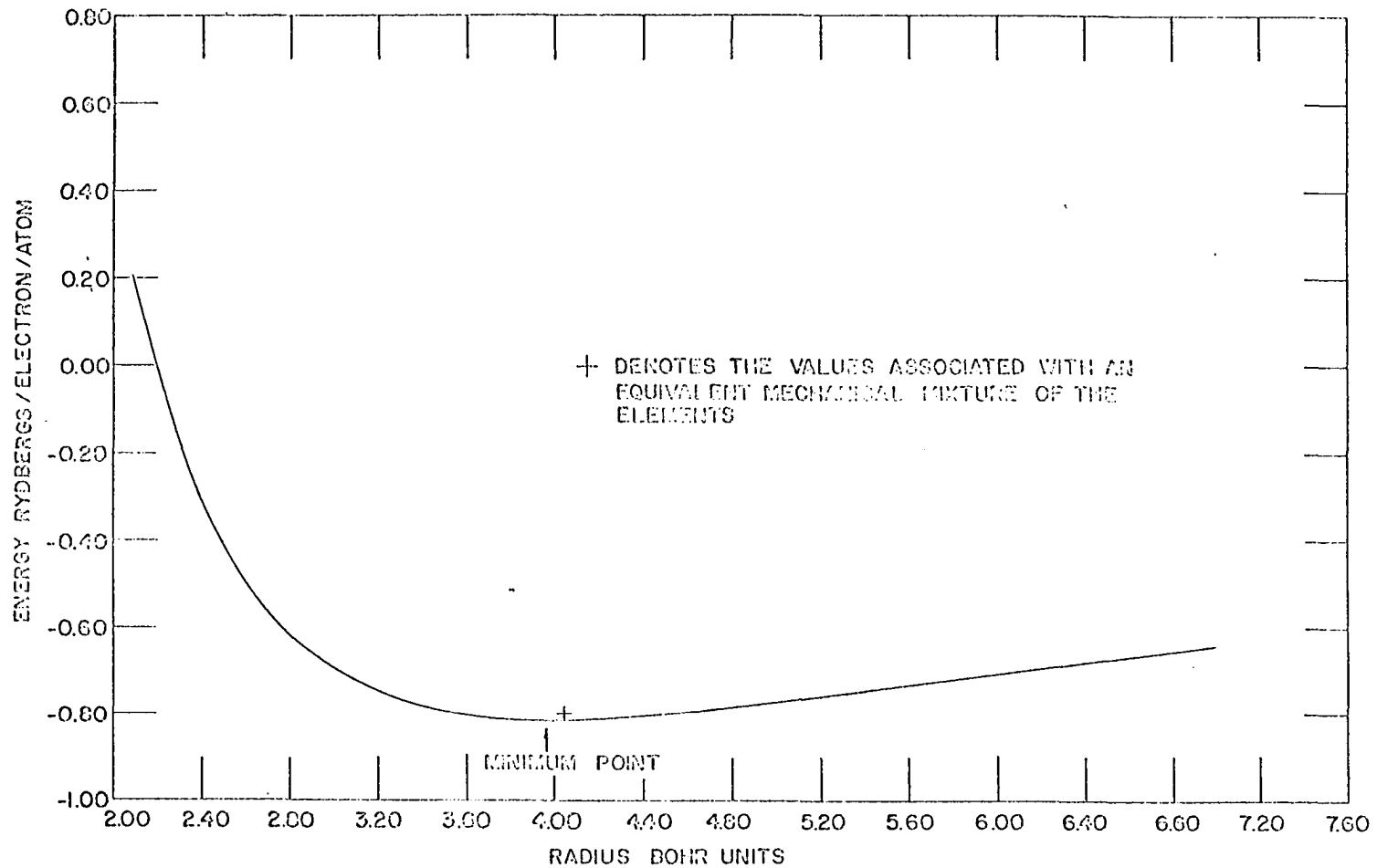


Figure 4. The cohesive energy of CaMg_2 as a function of the parameter, R of Equation 12, and with the ratio of $R_2/R_1 = \sqrt{1.5}$

determined for values of the ratio of R_2 to R_1 between 1.0 and 10.0. These data are presented in Figures 5a and 5b and Table 9. When both parameters are considered as free variables, the minimum in the cohesive energy relation yields a value of approximately -172 K cal/gram atom for the enthalpy of formation of CaMg_2 and a volume expansion on the order of 40 times the volume of the elements.

The value of the radius ratio at the minimum was found to be 7.68. When these values associated with the minimum in the cohesive energy are compared to the experimental values, they are found to be quite unrealistic. The volume associated with the Wigner-Seitz cell of calcium in the compound was found to be on the order of 75 times the volume of the elemental metal, while the magnesium was observed to contract on alloying to approximately one-third of its elemental size. Similar behaviour was observed when the calculations were extended to the compounds, SrMg_2 and BaMg_2 . The preceding calculations of the enthalpies of formation and the equilibrium volumes, were also carried out with the R_0 's fixed at the values obtained by Brooks (1963) who employed the Quantum Defect Method to calculate the cohesive energies of a number of elements. Although his calculated cohesive energies give

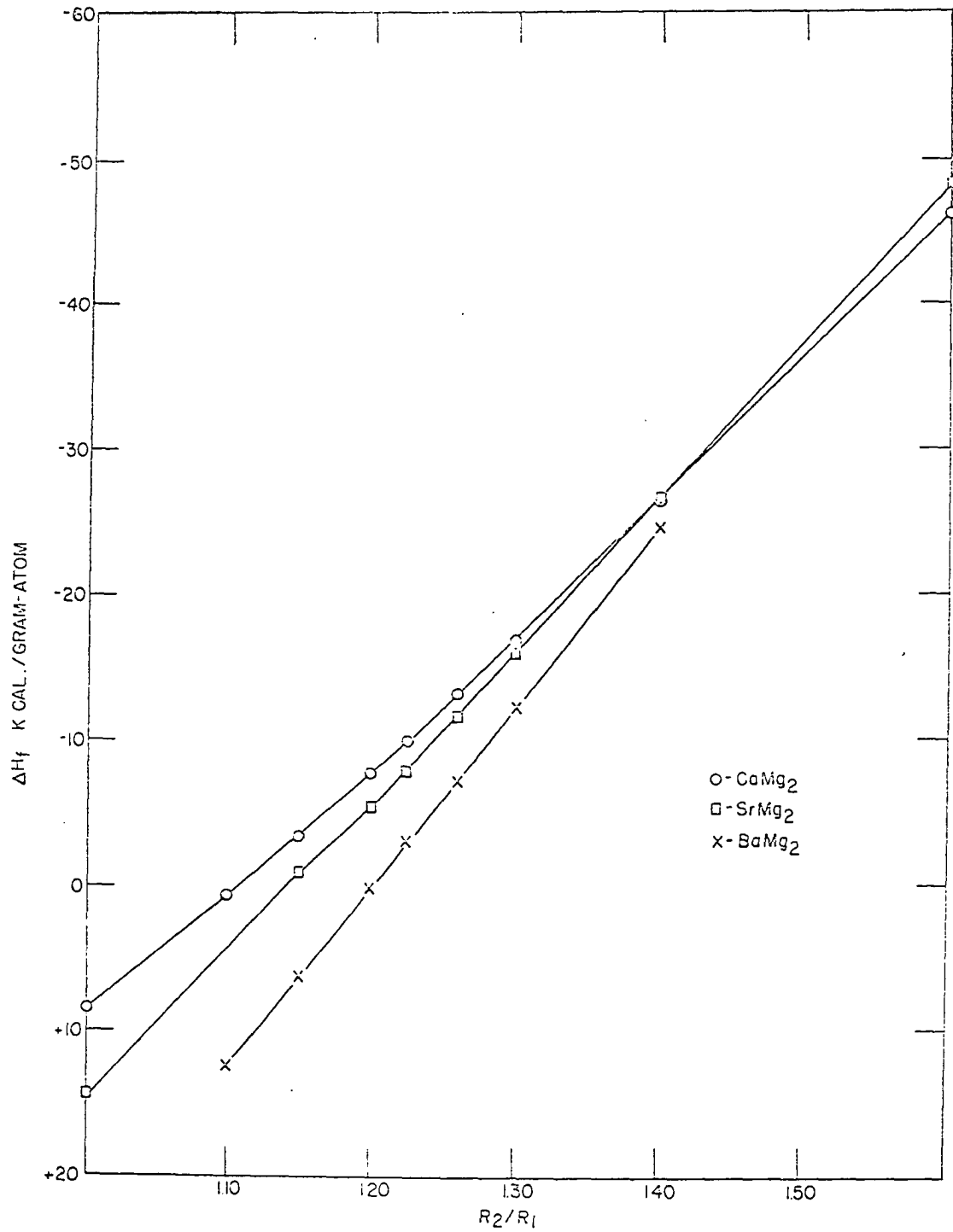


Figure 5a. The enthalpies of formation of CaMg₂, SrMg₂, and BaMg₂ as functions of the size ratio

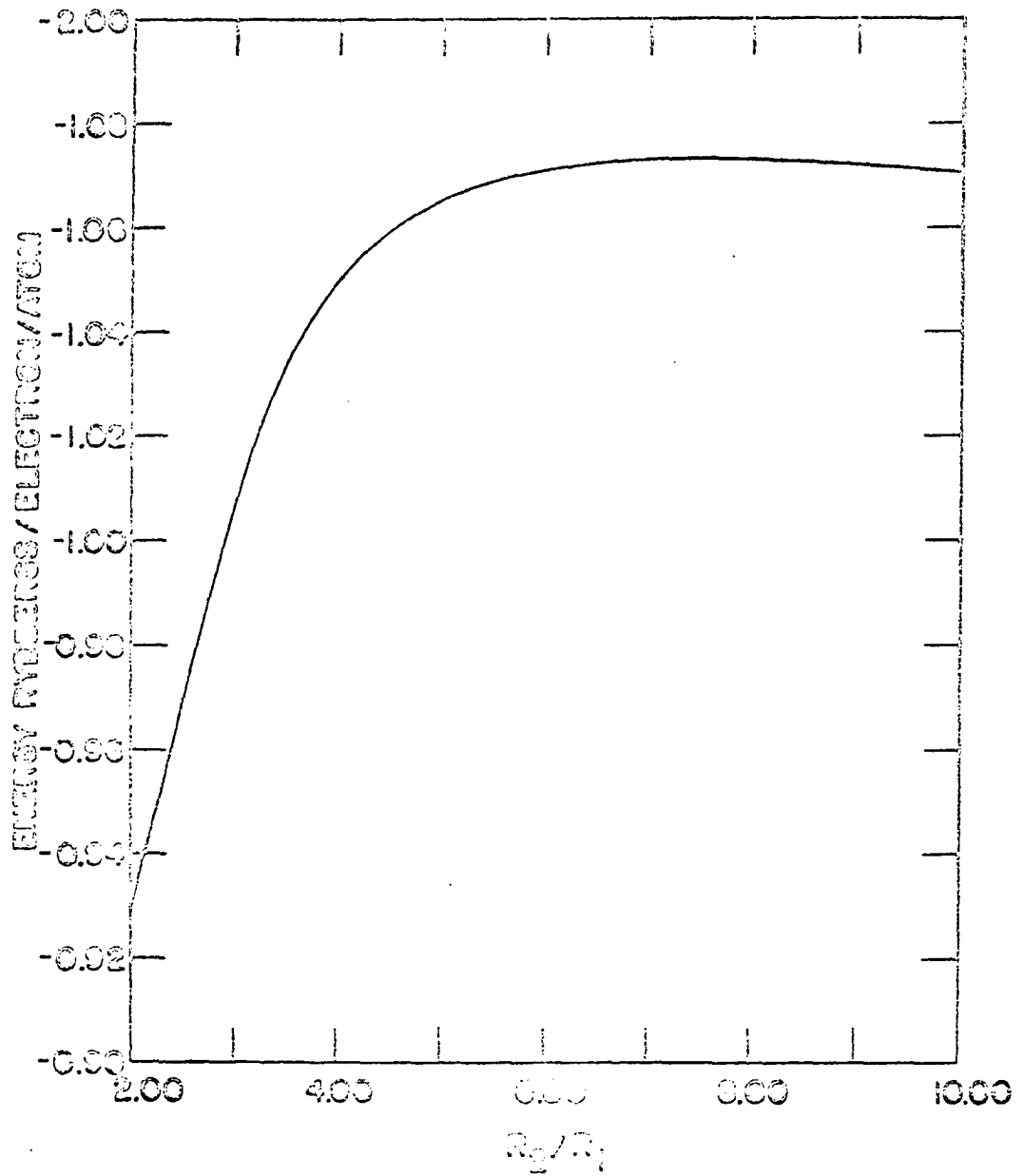


Figure 5b. A plot of the cohesive energy of CaMg₂ versus the size ratio

better agreement for the elements than the values calculated by Raines, no improvement was noted in the calculated values of the enthalpies of formation. The results of these two calculations are compared in table 10.

A much more realistic partition of the volumes was obtained from a consideration of the crystal structure of these compounds and the resulting size ratio gave a much better agreement between the calculated and measured values. Laves (1956) has observed that the value of the size ratio of the C15 structure is $\sqrt{1.5}$. To obtain this value, the interatomic distance between like nearest neighbor atoms was taken as a measure of the size of the respective atomic species in the compound. The ratio of these distances then yields the desired value of $\sqrt{1.5}$. Laves suggests this value as the ideal ratio of the constituents not only for the C15 structures but also the C14 structures. The compounds of interest here have been observed to possess the symmetry of the C14 crystal structure. The C14 and the C15 structures are related in the same manner that the hexagonal closest packed structure is related to the closest packed face centered cubic structure. Laves has further observed that the ratio of the Goldschmidt radii of the respective elements has the mean value of 1.225

for a statistical sample of 76 compounds with these crystal structures.

Rudman (1965) has suggested a one for two substitutional scheme for these structures. The ideal size ratio is based on volume considerations and leads to an ideal radius ratio of $(2)^{1/3}$. He also postulates that systems which deviate from this ideal ratio should exhibit a strain energy contribution to the thermodynamics of formation. Such an interpretation is also suggested by the data of King and Kleppa (1964). Their measurements of the heats of formation of CaMg_2 , SrMg_2 , and BaMg_2 indicate that CaMg_2 with a size ratio close to ideality has the largest heat of formation, and that BaMg_2 whose size ratio is the least favorable of the three compounds also has the smallest heat of formation.

The size ratios were fixed at the values suggested by Laves and Rudman and the resulting values for the heats of formation and the volume contractions are summarized for CaMg_2 , SrMg_2 , and BaMg_2 in Table II. The agreement between the cohesive energies are much better than the agreement between the heats of formation. This is not too surprising since the heats of formation were obtained as the differences between the calculated cohesive energies and these

differences are on the order of one percent of the cohesive energy values.

Although the simple model that formed the basis of these calculations precludes exact agreement with the experimental values, the results are in reasonable agreement and more important the order of the decrease of the stability of the series CaMg_2 , SrMg_2 , and BaMg_2 is correctly reproduced.

Table 8. The enthalpy of formation of CaMg₂

$-\Delta H_f^\circ$ kcal/gm-atom	Temp. K ^o	$-\Delta H_f^\circ$ kcal/gm-atom	Reference
2.8 ± 1.0	655-718	2.7	Smith & Smythe (1959)
3.55 ± .38	440-511	3.49	Chiotti <i>et al.</i> (1964)
3.12	532	3.05	Gartner (1965)
3.23 ± .10	298	3.21	King & Kleppa (1964)
3.14 ± .21	298	<u>3.12</u>	Davison (1964)
average = 3.19			

Table 9. The enthalpy of formation and the volume change of formation of CaMg₂ calculated from Equation 14 as a function of R₂/R₁

R ₂ /R ₁	$-\Delta H_f$ kcal/gm-atom	$\frac{\Delta V_f}{\sum N_A V_A}$	Requil. Bohr units
1.00	-8.45	-.0167	4.05
1.10	- .81	-.0494	3.97
1.15	3.31	-.0566	3.96
1.20	7.64	-.0562	3.96
1.30	16.8	-.0458	3.97
1.40	26.4	-.0204	4.01
1.60	45.9	.0702	4.13
2.0	81.4	.403	4.55
3.0	135.	2.0	5.84
4.0	158.	5.1	7.41
5.0	167.	10.3	9.07
6.0	171.	17.9	10.8
7.0	172	28.5	12.5
8.0	172	42.5	14.2
9.0	171.	60.4	15.9
10.0	171.	82.8	17.6

Table 10. The calculated heats of formation with $R_2/R_1 = \sqrt{1.5}$

R_0 (Bohr units)				Reference for R_0	$-\Delta H_f$ kcal/gm-atom		
Mg	Ca	Sr	Ba		CaMg ₂	SrMg ₂	BaMg ₂
2.56	3.49	3.83	4.33	Raines (1952)	+9.84	7.88	2.84
2.39	3.23	3.53	3.90	Brooks (1963)	11.01	9.39	5.69

Table 11. A comparison of the experimental and calculated values of the cohesive energy, E, and some related properties

	$-\Delta H_f$			$-E$			$-\frac{\Delta V_f}{\sum_A \frac{N_A V_A}{A}}$			$B \times 10^{12}$	
	kcal/gm-atom		exp.	kcal/gm-atom		exp.	calculated		exp.	dynes/cm ²	
	A	B		A	B		A	B		A	exp.
CaMg ₂	9.8	13.0	3.2	510.5	513.7	527.4	.0566	.0530	.0566	.265	.377 ^b
SrMg ₂	7.9	11.6	1.7	499.2	503.0	515.2	.0964	.0980	.0842		
BaMg ₂	2.8	7.2	0.5	482.6	487.0	502.4	.1535	.1590	.0703		

^aThe values of columns labeled A are with $R_2/R_1 = (1.5)^{1/2}$ and the values of columns labeled B are with $R_2/R_1 = (2)^{1/3}$.

^bThe bulk modulus of CaMg₂ was obtained by Sumer and Smith (1962).

SUMMARY

The heat capacity of CaMg_2 has been measured from 4.9°K to 286.6°K with an adiabatic calorimeter. The standard entropy of CaMg_2 was evaluated from these data in accordance with the Third Law of Thermodynamics to obtain a value of $8.27 \text{ cal/gm-atom/K}^\circ$ at 298.1°K . This value was combined with the existing entropy values of the appropriate elements to yield a value of $-.25 \pm .06 \text{ cal/K}^\circ/\text{gm-atom}$ for the standard entropy of formation of CaMg_2 at 298.1°K .

The heat content of CaMg_2 was measured with the aid of a Bunsen ice calorimeter from 273°K to 670°K . These data were combined with the heat capacity information and existing data for the standard enthalpy of formation of CaMg_2 and the heat capacities of the elements to obtain a value of -3.19 Kcal/mole for the standard enthalpy of formation at 0°K .

The cohesive energies of CaMg_2 , SrMg_2 , and BaMg_2 were evaluated in the framework of the free electron theory of metals. The ground state energies of the valence electrons of the compounds were approximated as the arithmetic mean of the ground state energies of the appropriate elements. The states of higher energy were calculated in the free electron approximation. With the size ratio of the constituents fixed at the

value of 1.125, a value suggested by the crystal structure of the compound, the enthalpies of formation of CaMg_2 , SrMg_2 , and BaMg_2 were calculated. Although this simple model precludes an exact quantitative agreement between the calculated and experimental values, the results are in reasonable accord and the order of decreasing stability of the series CaMg_2 , SrMg_2 , and BaMg_2 is correctly reproduced.

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