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# The single crystalline elastic constants for the MgCu<sub>2</sub>-MgZn<sub>2</sub> system

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OF THE  $\text{MgCu}_2$ - $\text{MgZn}_2$  SYSTEM.

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THE SINGLE CRYSTALLINE ELASTIC CONSTANTS  
OF THE  $\text{MgCu}_2\text{-MgZn}_2$  SYSTEM

by

Gary Wayne Shannette

A Dissertation Submitted to the  
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## INTRODUCTION

## Laves Phases

An appreciable amount of work has been done to elucidate the factors (1,2) that influence the stability of the large group of intermetallic compounds known as "Laves Phases." The three different structure types of Laves phases are C14, C15, and C36 in the Strukturbericht notation (3) and their prototype structures are MgZn<sub>2</sub>, MgCu<sub>2</sub>, and MgNi<sub>2</sub>, respectively. All three structures have the general formula AB<sub>2</sub>. The atomic array in these structures may be understood by considering the sublattices of the A and B atoms separately. Figure 1 shows the positions of the A and the B atoms in their sublattices, and it also shows how the interpenetrating sublattices fit together to form the composite lattice with a basis. The MgCu<sub>2</sub> and the MgZn<sub>2</sub> structures have XYZXYZ and XYXYXY layering, respectively. The MgNi<sub>2</sub> structure contains both of these types of layering, and this results in a stacking sequence of XYXZXYXZ (4). A more complete description of the structures of the Laves phases is given in the excellent review article by Berry and Raynor (5). In the ideal case the radius ratio of these phases is  $r_A/r_B = 1.225$  and geometrical considerations indicate that atomic size is the dominant

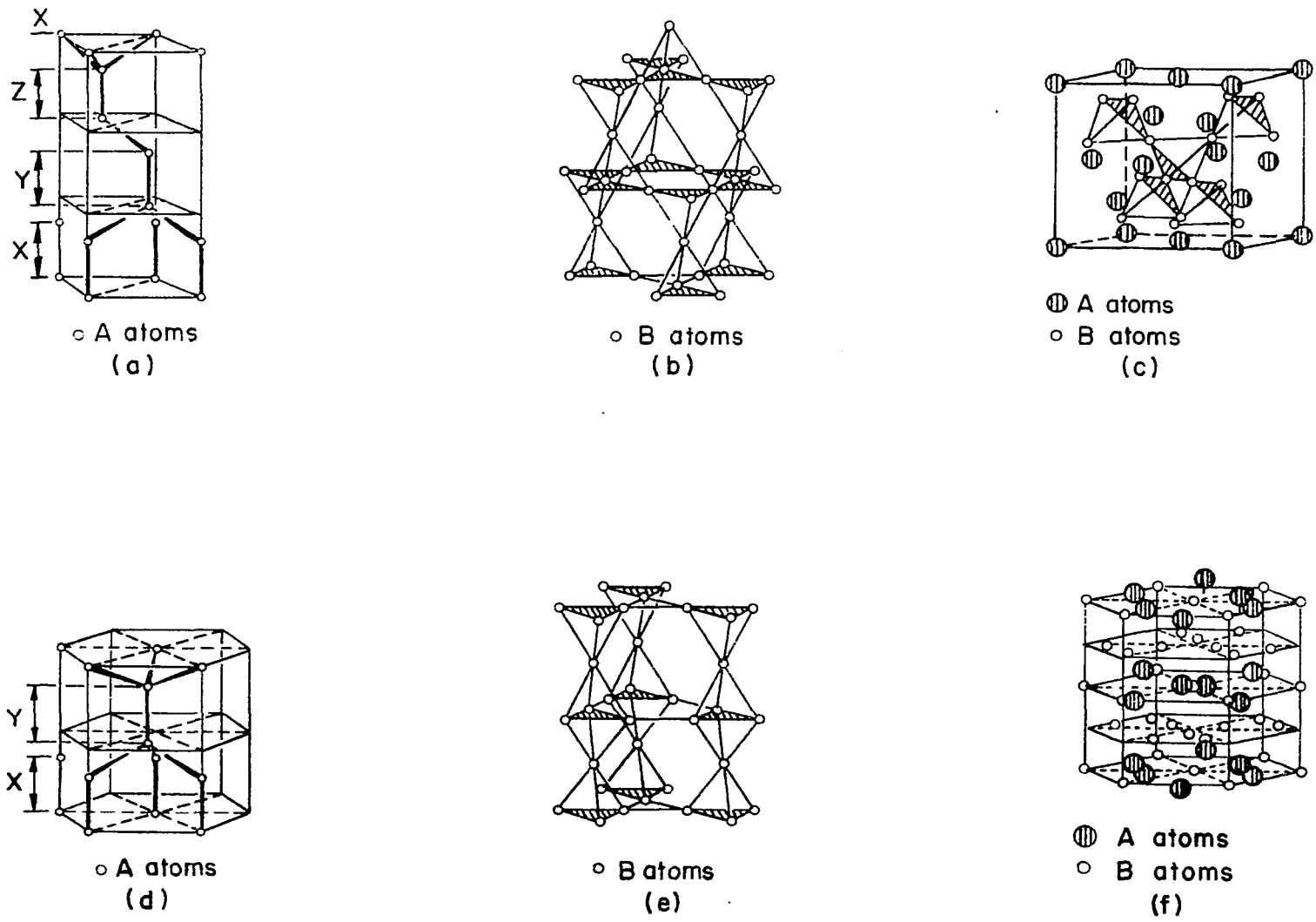


Figure 1. Atomic arrays of Laves phases  
 (a) Sublattice of large A atoms in  $MgCu_2$ , (b) Sublattice of small B atoms in  $MgCu_2$ , (c) Composite lattice of  $MgCu_2$ , (d) Sublattice of large A atoms in  $MgZn_2$ , (e) Sublattice of small B atoms in  $MgZn_2$ , (f) Composite lattice of  $MgZn_2$

factor in the stability of Laves phases (2). However, past studies have shown that while the size effect is important in determining whether or not a Laves phase forms, the particular structure type that is stable is determined to a large extent by electronic considerations (2).

The system chosen for this investigation is the  $\text{MgCu}_2$ - $\text{MgZn}_2$  quasi-binary system. All three Laves phase structures exist in this system as is shown in the phase diagram in the top section of Figure 2. Laves and Witte (6) have discussed the possibility that there is a certain range of electron/atom ratios over which a particular Laves phase structure would be expected to be stable. They found the  $\text{MgCu}_2$  structure would be expected to be stable for electron/atom ratios of 1.33 to 1.80, the  $\text{MgNi}_2$  structure from 1.80 to 1.95, and the  $\text{MgZn}_2$  structure from 1.95 to 2.2. The  $\text{MgCu}_2$ - $\text{MgZn}_2$  system follows this scheme quite closely. Klee and Witte (7) have measured the magnetic susceptibility of these alloys. Their results, shown in the bottom section of Figure 2, indicate that there are changes in the electronic distribution in this system. Previous work on the lead-thallium system (8) has shown that the elastic constants are sensitive to changes in the electronic interactions. For this reason the  $\text{MgCu}_2$ - $\text{MgZn}_2$  system

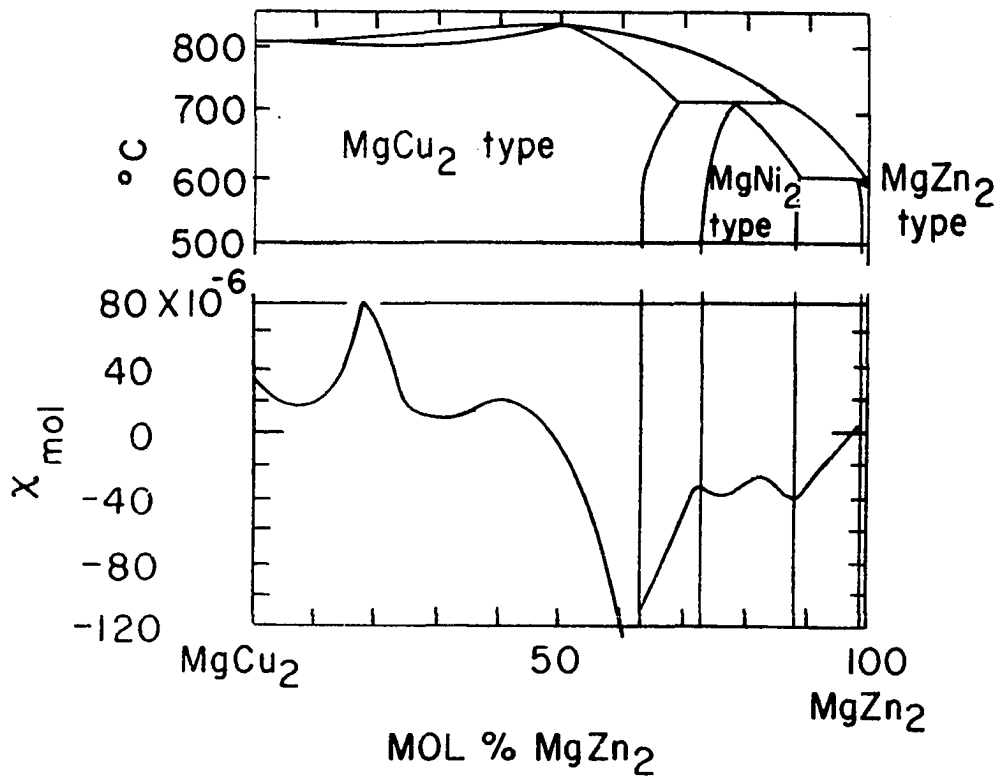


Figure 2. Phase diagram and magnetic susceptibility of the MgCu<sub>2</sub>-MgZn<sub>2</sub> system



was chosen for this investigation.

### Crystal Elasticity

The strains in a crystal are defined as

$$e_1 = \frac{\partial u}{\partial x}, \quad e_2 = \frac{\partial v}{\partial y}, \quad e_3 = \frac{\partial w}{\partial z},$$

$$e_4 = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}, \quad e_5 = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}, \quad e_6 = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}$$

where  $u$ ,  $v$ , and  $w$  are displacements and  $x$ ,  $y$ , and  $z$  are the position coordinates (9). The force acting on a unit area in the solid is defined as the stress. Hooke's Law states that for sufficiently small deformations the stress is directly proportional to the strain. This may be written in tensor notation as

$$\sigma_i = C_{ij}e_j \quad (i, j = 1, 2 \dots 6) \quad (1)$$

where  $\sigma_i$  is the homogeneous stress,  $e_j$  is the resulting homogeneous strain, and the proportionality constants ( $C_{ij}$ ) are the single crystalline elastic constants.

The First Law of Thermodynamics for an adiabatic process may be written as

$$dE = dW,$$

where  $dE$  is the change in internal energy and  $dW$  is the amount of work done on the system during the displacement

of a volume under stress. The work done may also be written

$$dW = \sigma_i de_i, \quad (i = 1, 2 \dots 6)$$

which with the application of Hooke's Law becomes

$$dE = dW = C_{ij} e_j de_i \quad (i, j = 1, 2 \dots 6).$$

Since  $dE$  is an exact differential then

$$\frac{d^2E}{de_i de_j} = C_{ij} = C_{ji} \quad (i, j = 1, 2 \dots 6).$$

This indicates that if the energy of a crystal is known as a function of strain the elastic constants may be calculated.

Also the fact that  $C_{ij} = C_{ji}$  reduces the number of independent elastic constants of Equation 1 from 36 to 21. Symmetry constraints of the crystal structures further reduce the number of independent elastic constants to five for the hexagonal system and three for the cubic system (10).

## EXPERIMENTAL PROCEDURE

## Crystal Preparation

Six single crystals of the ternary cubic Laves phase  $\text{Mg}(\text{Cu},\text{Zn})_2$  were grown for this investigation. The materials which were employed were: Bunker Hill slab zinc, 99.99% pure; American Smelting and Refining copper, 99.999% pure; and Ames Laboratory magnesium with a typical analysis of 13 ppm nitrogen, 195 ppm carbon, and trace amounts of calcium, copper, nickel, and silicon. The copper and zinc were cleaned in dilute solutions of  $\text{HNO}_3$  and  $\text{HCL}$ , respectively, while the magnesium required no surface cleaning since it had been stored under an inert atmosphere. Graphite crucibles were degassed in a vacuum of less than one micron for 1/2 hour at approximately  $1000^\circ\text{C}$ . The stoichiometric amounts of the copper, zinc, and magnesium were placed in the crucibles with zinc, the component with the lowest melting point, being placed on top of the charge to insure early alloy formation in the melting process. Each crucible was then placed on a water-cooled pedestal in a resistance furnace. This Bridgman apparatus for growing the single crystals is essentially the same as the one described by Morris, Redin, and Danielson (11). The heating chamber was next evacuated for a minimum

of 4 hours to remove any air from around the sample. The furnace was then heated slowly ( $50^{\circ}\text{C}$  per hour) to approximately  $300^{\circ}$  in vacuo to allow further degassing of the crucible. Next the heating chamber was pressurized with helium to 28 psi to help prevent the loss of zinc. The heating was continued until the temperature of the sample was approximately  $100^{\circ}\text{C}$  above the melting point of the alloy. The sample was held at this temperature for three hours to facilitate homogenization and was then slowly cooled at a rate of  $5^{\circ}\text{C}$  per hour. The water-cooled pedestal provided a temperature gradient of approximately  $30^{\circ}\text{C}$  per inch at temperatures near the melting point of the samples. When the temperature was approximately  $200^{\circ}\text{C}$  below the melting point, the cooling rate was increased to  $20^{\circ}\text{C}$  per hour. This relatively slow cooling rate was necessary since faster cooling rates caused the samples to crack. The samples had a rough surface when removed from the crucible, and it was difficult to see if any grain boundaries were present. Therefore, the samples were confirmed to be single crystals by a Laue back-reflection technique. Each sample was found to be completely a single crystal except for a small region near the top of the sample. Debye-Scherrer powder patterns were taken in order to insure

that each sample was of the proper phase and that no second phase was present. The homogeneity of the samples was established by chemical analyses of the top and bottom of two of the crystals. The analyses indicated that the composition within a given crystal was uniform to within  $\pm 0.5$  weight per cent. Additional chemical analyses were made on all samples to establish the composition of the specimens that were employed in the elastic constant measurements. These results are given in Table 1. The samples of the latter chemical analyses were culled from excess material remaining after the test specimens were procured.

Table 1. Chemical composition, lattice parameters, and x-ray densities of  $\text{Mg}(\text{Cu},\text{Zn})_2$  alloys

Mole percent $\text{MgZn}_2$	Lattice parameter ( $\text{\AA}$ )	Density (gm/cc)
9.99	$7.062 \pm .0005$	5.780
19.00	$7.093 \pm .0005$	5.673
22.63	$7.110 \pm .0005$	5.606
27.34	$7.116 \pm .0005$	5.618
36.70	$7.148 \pm .0005$	5.534
50.11	$7.173 \pm .0005$	5.481

The stoichiometries of the samples were checked and the maximum deviation from the ideal  $\text{AB}_2$  composition was less than 1.3 atom per cent. A single crystal of  $\text{MgZn}_2$  was ordered from

Semi-Elements, Inc. This sample contained several grain boundaries. However, it was possible to cut single crystals from the large grains. A chemical analysis was performed on this sample to insure that the composition of the sample corresponded to  $\text{MgZn}_2$ .

The crystallographic orientations in the crystals were determined by the Laue back-reflection method. For this purpose the crystals were mounted on a two-circle goniometer with a mixture of Duco cement and graphite powder. After the appropriate axis had been located, the goniometer and crystal were transferred to a Sparcatron electromachining apparatus. This procedure enabled the cutting of two parallel faces whose normals were within  $\pm 0.5^\circ$  of the desired axis. The cubic crystals were cut so that the parallel faces were perpendicular to the  $[110]$  axis. In hexagonal  $\text{MgZn}_2$  parallel faces were cut  $0^\circ$ ,  $90^\circ$ , and  $42.8^\circ$  to the C-axis. The faces were then hand lapped on 600 grit metallographic paper to obtain faces that were parallel to within  $\pm 0.0003$  cm. The samples were x-rayed again to insure that the faces were not misaligned and that there was no evidence of worked metal. The finished cubic  $\text{Mg}(\text{Cu},\text{Zn})_2$  samples were nearly circular in cross-section with a minimum diameter of  $1/2''$  and a minimum thickness of

1/4". The MgZn<sub>2</sub> samples were irregular in cross-section with a minimum width of 3/8" and a minimum thickness of 1/4".

The densities of the crystals were obtained from precision lattice parameters determined by a back-reflection focusing technique. The lattice parameters and the calculated x-ray densities are included in Table 1. Leiser and Witte (12) have also measured the lattice parameters of these alloys and the agreement between the two sets of data is within the experimental precision of the measurements.

#### Acoustic Measurements

The elastic constants are related to the velocity of sound by the following relationship

$$C = \rho V^2, \quad (2)$$

where  $\rho$  is the crystal density and  $C$  is the appropriate combination of  $C_{ij}$ 's, the conventional elastic constants, corresponding to the particular polarization and direction of wave propagation associated with the velocity,  $V$ . The ultrasonic pulse-echo technique (13) was used to determine the transit time of the sonic waves and the transit times can be readily converted into velocities through a knowledge of the dimensions of the sample.

In the case of cubic crystals the three independent

single crystalline elastic constants may be determined by the measurement of the transit times of a longitudinal and two transverse waves propagated in the  $[110]$  direction (9). The elastic constants may then be calculated from the velocities by the following relations:

$$\rho V_t^2 = C_{44}, \quad (3)$$

$$\rho V_t'^2 = C' = \frac{1}{2}(C_{11}-C_{12}), \quad (4)$$

$$\rho V_l^2 = C_L = \frac{1}{2}(C_{11}+C_{12}+2C_{44}), \quad (5)$$

where  $V_t$  is the velocity of a transverse wave polarized in the  $[001]$  direction,  $V_t'$  is the velocity of a transverse wave polarized in the  $[\bar{1}10]$  direction, and  $V_l$  is the velocity of the longitudinal wave. For the hexagonal case the elastic constants of Equation 2 are related to the conventional elastic constants in the following way (14,15):

$$C_L(\theta) = \frac{1}{2}(C_{11}+C_{44})\sin^2\theta + \frac{1}{2}(C_{33}+C_{44})\cos^2\theta + \emptyset(C_{ij},\theta),$$

$$C_T^I(\theta) = \frac{1}{2}(C_{11}+C_{44})\sin^2\theta + \frac{1}{2}(C_{33}+C_{44})\cos^2\theta - \emptyset(C_{ij},\theta),$$

$$C_T^{II}(\theta) = \frac{1}{2}(C_{11}-C_{12})\sin^2\theta + C_{44}\cos^2\theta,$$

with

$$\begin{aligned} \emptyset(C_{ij},\theta) = & \frac{1}{2}\left\{(C_{11}-C_{44})^2\sin^4\theta + (C_{33}-C_{44})^2\cos^4\theta \right. \\ & \left. + 2\sin^2\theta\cos^2\theta[(C_{11}-C_{44})(C_{44}-C_{33}) + 2(C_{13}+C_{44})^2]\right\}^{\frac{1}{2}}, \end{aligned}$$



where  $\theta$  is the angle between the direction of wave propagation and the C axis. These three equations correspond to the three independent wave polarizations.

Quartz X and Y-cut transducers with a resonant frequency of 10 MHz generated the longitudinal and transverse pulses, respectively. The Y-cut transducers were cemented to the crystals with the following bonding agents: Dow Corning 200 Fluid for measurements at 4.2<sup>o</sup>K and 77<sup>o</sup>K, Nonaq Stopcock Grease for measurements from 90<sup>o</sup>K to 270<sup>o</sup>K, and Salol for measurements at 273<sup>o</sup>K and 298<sup>o</sup>K. The X-cut transducers were bonded to the crystals with Nonaq Stopcock Grease for all the measurements. Problems were encountered in obtaining satisfactory bonds in the 80-100<sup>o</sup>K temperature range with both X-cut and Y-cut transducers; however, the best results were finally achieved by applying a very thin layer of bonding agent to the back face of the transducer.

## EXPERIMENTAL RESULTS

The elastic constants were measured in the temperature range of 77°K to 298°K and several measurements were made at 4.2°K to check the extrapolation to 0°K. The directly measured elastic constants are plotted in Figures 3, 4, 5, and 6 and the values resolved from the smoothed curves are given in Tables 2 and 3. The precision of the elastic constant measurements is based on the fact that the transit times could be determined to  $\pm 0.005$  microsecond and this results in precisions which vary from 0.2% to 0.5% for the directly measured elastic constants. Several sources of systematic errors, such as the precision of the thickness measurements, non-parallelism in the crystal faces, errors in the density determinations due to errors in the lattice parameter and chemical composition, and misalignment from the desired crystallographic axis, do exist. An estimation of each of these errors leads to a maximum total non-random error of less than 1% at room temperature. For measurements made at temperatures below room temperature, another systematic error exists due to the thermal contraction of the sample. There are no thermal expansion data available for these alloys but thermal expansion data do exist for MgCu<sub>2</sub> (16). From these data it can be

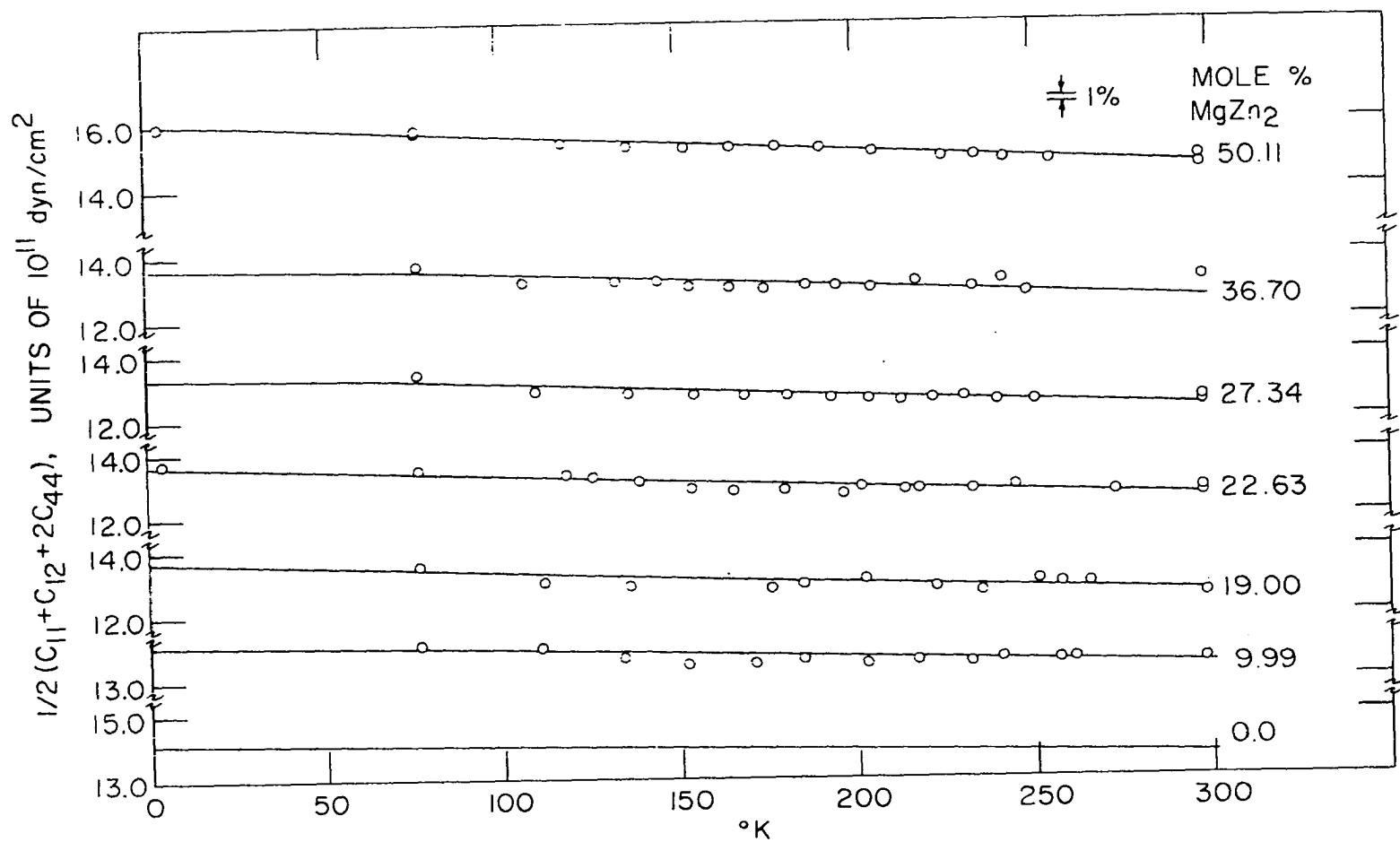


Figure 3. The adiabatic elastic constants  $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$  as a function of temperature for the cubic  $Mg(Cu,Zn)_2$  Laves phases

Figure 4. The adiabatic elastic constants  $\frac{1}{2}(C_{11}-C_{12})$  as a function of temperature for the cubic  $\text{Mg}(\text{Cu},\text{Zn})_2$  Laves phases

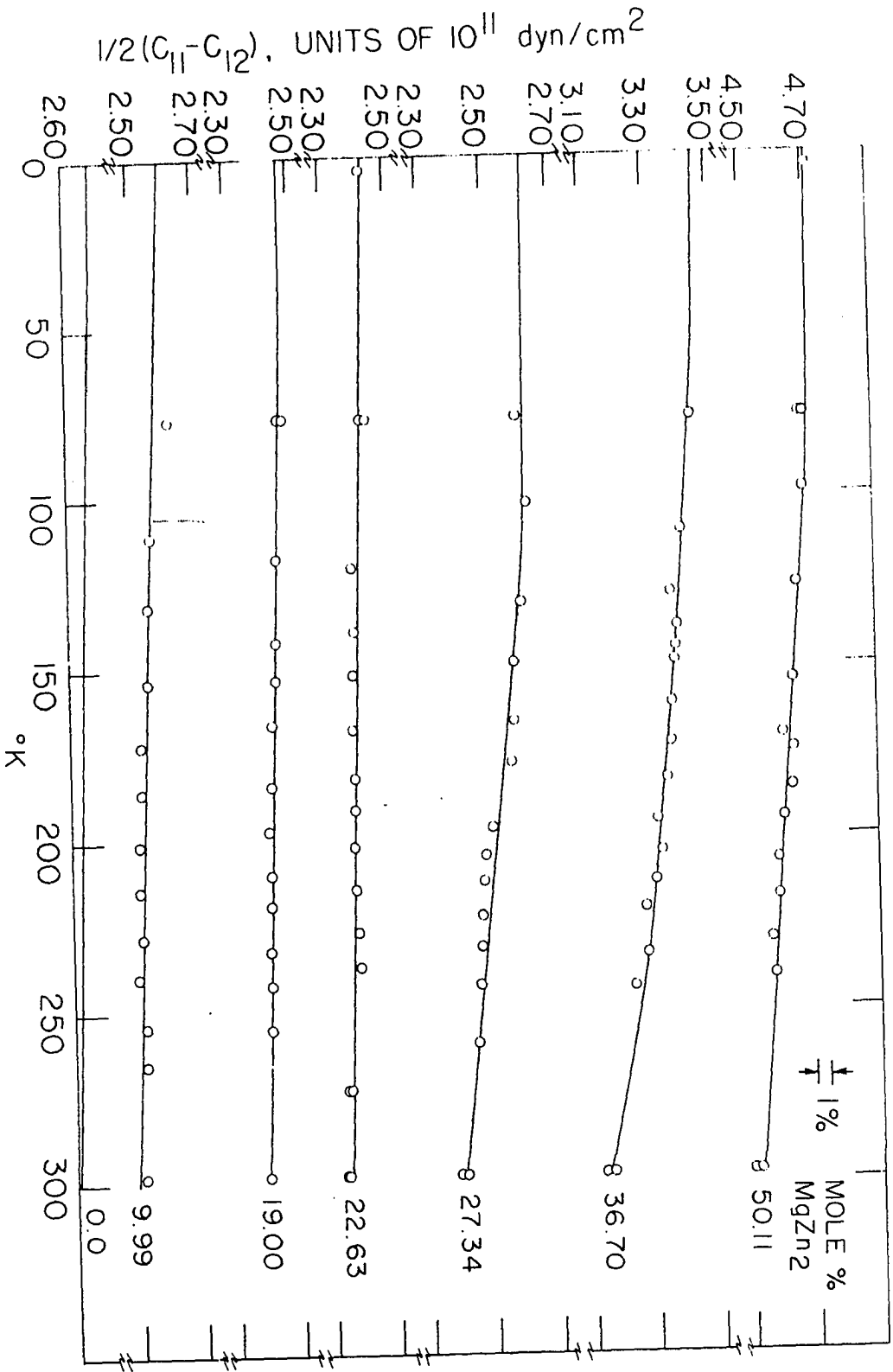
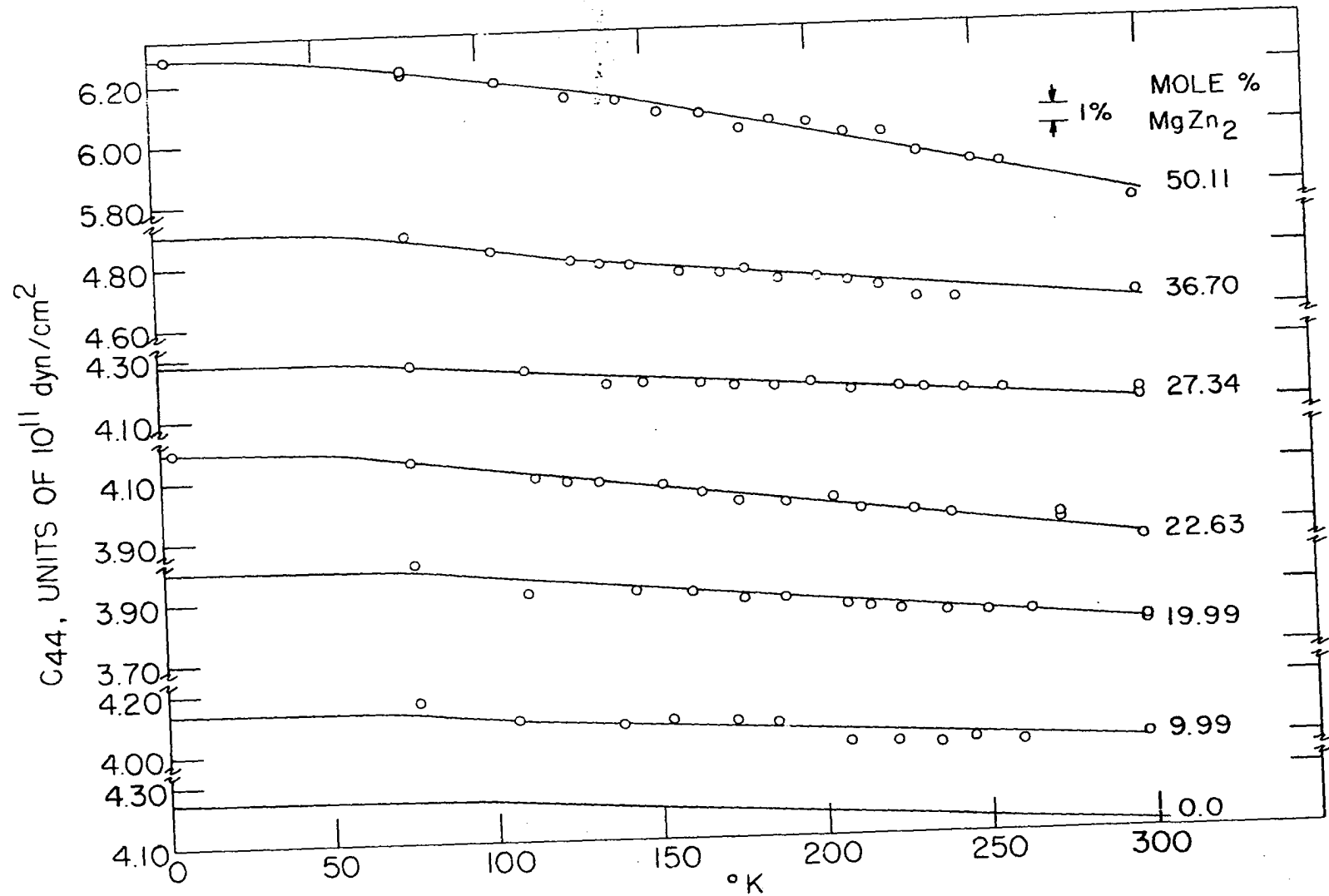


Figure 5. The adiabatic elastic constants  $C_{44}$  as a function of temperature for the cubic  $\text{Mg}(\text{Cu},\text{Zn})_2$  Laves phases



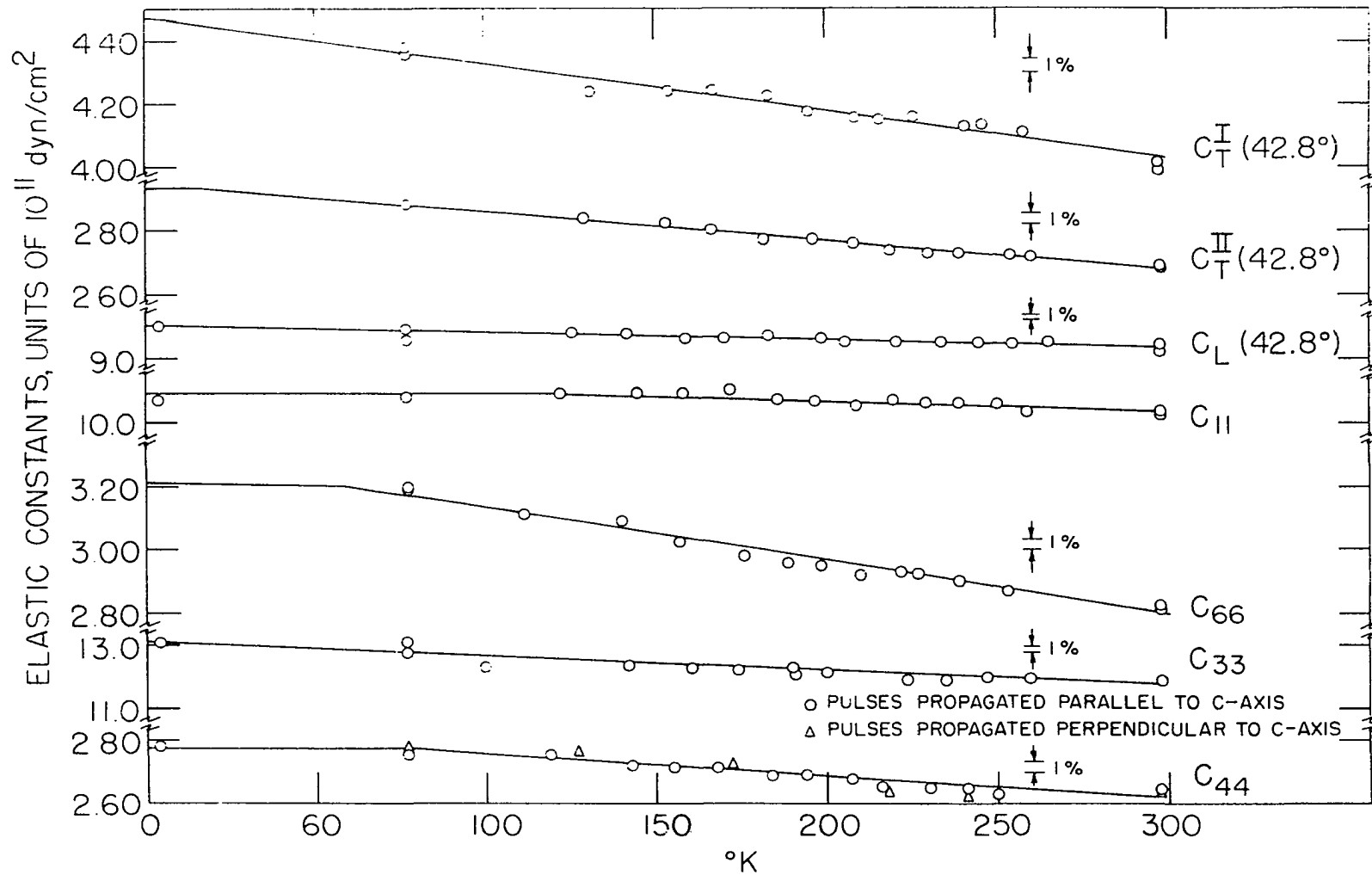


Figure 6. The adiabatic single crystalline elastic constants of MgZn<sub>2</sub> as a function of temperature



Table 2. Adiabatic elastic constants of MgCu<sub>2</sub>-MgZn<sub>2</sub> cubic Laves phases in units of 10<sup>11</sup>dynes/cm<sup>2</sup>

Mol % MgZn <sub>2</sub>	Temp. (°K)	C <sub>L</sub>	C <sub>44</sub>	C'	C <sub>11</sub>	C <sub>12</sub>
9.99	0	14.10	4.140	2.600	12.56	7.360
	50	14.00	4.131	2.581	12.45	7.288
	100	13.98	4.103	2.560	12.44	7.317
	150	13.83	4.071	2.591	12.35	7.168
	200	13.70	4.045	2.526	12.18	7.129
	250	13.59	4.020	2.509	12.08	7.061
	300	13.50	3.992	2.490	11.99	7.018
19.00	0	13.68	4.000	2.470	12.150	7.210
	50	13.52	3.998	2.470	11.992	7.052
	100	13.60	3.968	2.455	12.087	7.177
	150	13.12	3.920	2.440	11.740	6.860
	200	12.99	3.873	2.425	11.542	6.692
	250	12.78	3.828	2.410	11.362	6.542
	300	12.67	3.782	2.396	11.284	6.492
22.63	0	13.62	4.190	2.430	11.860	7.000
	50	13.45	4.185	2.422	11.687	6.843
	100	13.29	4.120	2.410	11.580	6.760
	150	13.11	4.052	2.398	11.456	6.660
	200	12.93	3.989	2.380	11.321	6.561
	250	12.75	3.923	2.368	11.195	6.459
	300	12.60	3.857	2.350	11.093	6.393
27.34	0	13.30	4.280	2.620	11.640	6.400
	50	13.22	4.270	2.620	11.570	6.330
	100	13.08	4.242	2.610	11.448	6.228
	150	12.89	4.208	2.572	11.254	6.110
	200	12.68	4.171	2.514	11.023	5.995
	250	12.50	4.139	2.458	10.819	5.903
	300	12.32	4.101	2.400	10.619	5.819

Table 2. (Continued)

Mol % MgZn <sub>2</sub>	Temp. (°K)	C <sub>L</sub>	C <sub>44</sub>	C'	C <sub>11</sub>	C <sub>12</sub>
36.70	0	13.60	4.900	3.450	12.150	5.250
	50	13.56	4.900	3.450	12.110	5.210
	100	13.44	4.838	3.417	12.019	5.185
	150	13.22	4.776	3.375	11.819	5.069
	200	13.01	4.726	3.320	11.604	4.964
	250	12.80	4.678	3.250	11.372	4.872
	300	12.61	4.630	3.142	11.122	4.838
	50.11	0	15.99	6.285	4.710	14.415
50		15.81	6.257	4.706	14.259	4.847
100		15.60	6.192	4.690	14.098	4.718
150		15.34	6.110	4.648	13.878	4.582
200		15.10	6.000	4.606	13.706	4.494
250		14.87	5.889	4.567	13.548	4.414
300		14.66	5.775	4.526	13.411	4.359

Table 3. Adiabatic elastic constants of MgZn<sub>2</sub> hexagonal Laves phase in units of 10<sup>11</sup>dynes/cm<sup>2</sup>

Temp.	C <sub>11</sub>	C <sub>33</sub>	C <sub>44</sub>	$\frac{1}{2}(C_{11}-C_{12})$	C <sub>L</sub> (42.8°)	C <sub>T</sub> <sup>I</sup> (42.8°)	C <sub>T</sub> <sup>II</sup> (42.8°)	C <sub>12</sub>	C <sub>13</sub>
0	10.80	13.10	2.775	3.210	9.90	4.470	2.940	4.380	2.81
50	10.80	12.88	2.775	3.210	9.90	4.400	2.907	4.380	2.87
100	10.80	12.69	2.758	3.136	9.81	4.328	2.860	4.528	2.95
150	10.79	12.43	2.723	3.052	9.70	4.251	2.811	4.686	2.99
200	10.62	12.21	2.688	2.970	9.57	4.177	2.769	4.680	2.96
250	10.49	12.00	2.652	2.883	9.45	4.102	2.723	4.724	2.94
300	10.32	11.80	2.620	2.798	9.33	4.030	2.680	4.724	2.90

estimated that the maximum thermal expansion error for the cubic Laves phases is less than 0.9% at 4.2<sup>o</sup>K. The thermal expansion coefficient for MgZn<sub>2</sub> was estimated from handbook values of the thermal expansion coefficient of magnesium and zinc (17) and the maximum error for MgZn<sub>2</sub> was then estimated to be less than 0.7% at 4.2<sup>o</sup>K.

## DISCUSSION

## The Adiabatic Bulk Modulus

It has been postulated that the bulk modulus of an alloy or an intermetallic phase can be estimated as the arithmetic mean of the bulk moduli of the component elements (18). This relation has been shown to be correct to within a few per cent for several two-component systems (18) and in the present work this postulate has been extended to include a quasi-binary system. In general, the elastic properties of an aggregate of crystals, such as the polycrystalline bulk modulus, cannot be calculated exactly from the single crystalline elastic constants due to the constraints caused by the grain boundaries. However, Voigt (19) and Reuss (19) have suggested averaging processes that may be used in calculating the elastic properties of polycrystalline materials. In Voigt's averaging scheme strain is assumed to be uniform and the relations expressing the stress in a single crystal in terms of a homogeneous strain are averaged. Reuss assumes that stress is uniform and averages the relations expressing the strain in terms of a homogeneous stress. Hill (19) has shown that the Voigt and Reuss averaging processes represent the upper and lower limits, respectively, for the calculated

polycrystalline elastic properties. However, both Voigt and Reuss schemes yield the same expression for the bulk modulus of an aggregate of cubic crystals since a hydrostatic stress produces an isotropic volume change in polycrystalline cubic material. Therefore, the postulates of uniform stress or uniform strain that are assumed in Voigt and Reuss averaging are both true and thus, each process yields the relationship (20)

$$K = 1/3 (C_{11} + 2C_{12}),$$

where  $K$  is the bulk modulus for cubic material. For polycrystalline hexagonal samples the Voigt and Reuss values of the bulk modulus (20) are given by

$$K_V = 1/9[2C_{11} + C_{33} + 2C_{12} + 4C_{13}]$$

and

$$K_R = \frac{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}{2C_{33} + C_{11} + C_{12} - 4C_{13}},$$

where  $K_V$  and  $K_R$  are the respective Voigt and Reuss values for the bulk moduli.

Figure 7 shows the results of these calculations with the straight line representing the arithmetic mean bulk moduli and with the circles representing the experimental values. For  $MgZn_2$  the circle represents the arithmetic mean

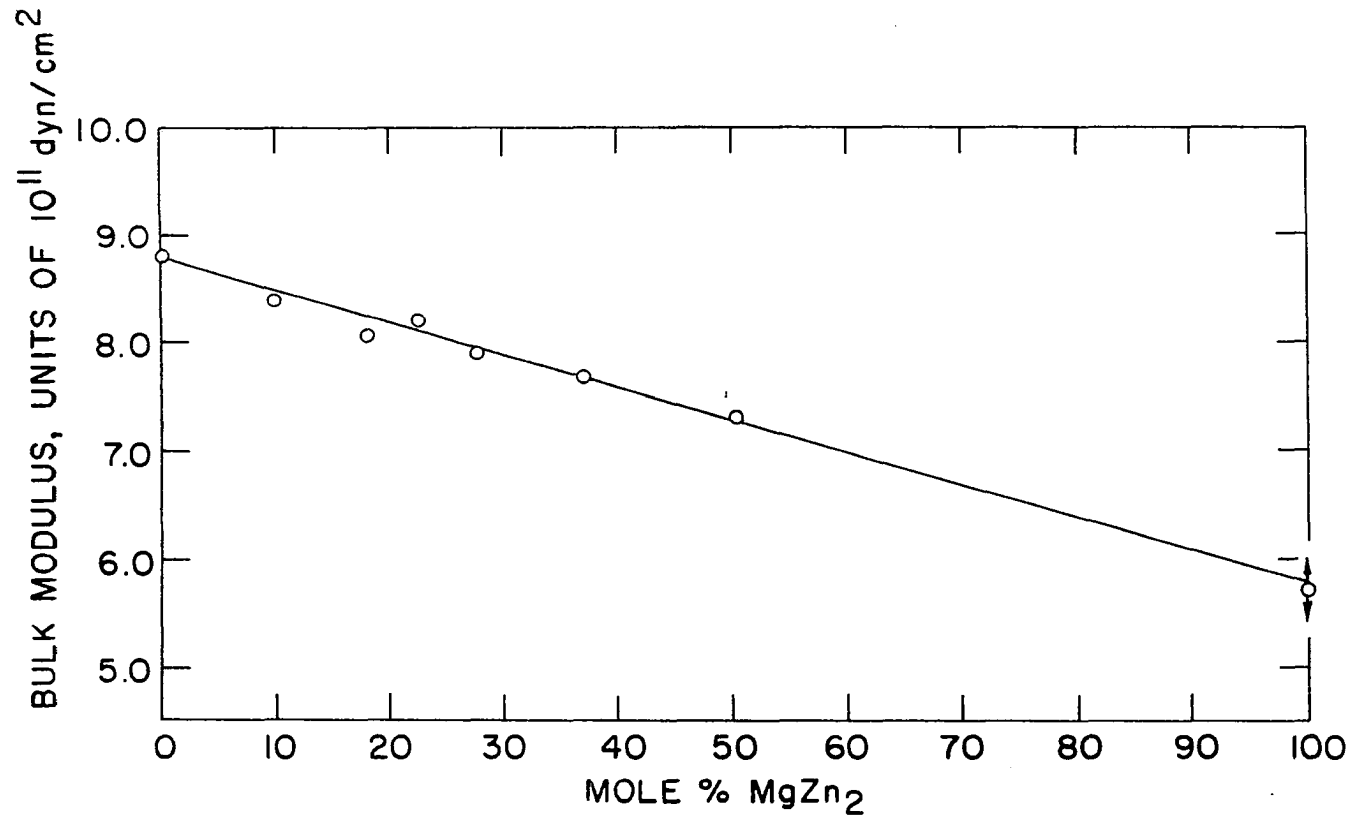


Figure 7. The arithmetic mean and the measured bulk moduli of the MgCu<sub>2</sub>-MgZn<sub>2</sub> system

bulk modulus. This value was obtained by averaging the bulk moduli of magnesium and zinc which were weighted in the proper stoichiometric ratio. The extremities of the error bar represent the Voigt and Reuss bulk moduli averaged from the single crystalline elastic constants of  $\text{MgZn}_2$ . Furthermore, this agreement verifies the arithmetic mean bulk modulus approximation and indicates that the approximation can probably be applied to systems containing several phases and three or more elements.

#### Interpretation of the Shear Constants

The composition dependence of the room temperature elastic constants has a minimum at approximately 20 mole%  $\text{MgZn}_2$  for all three directly measured elastic constants as shown in Figure 8. This composition corresponds to the first maximum in the magnetic susceptibility curve and hence to a maximum in the electronic density of states. Raynor (2) has suggested that this maximum is related to the fact that the Fermi surface touches the  $\{311\}$  faces of the Brillouin zone boundaries at this composition. Since the elastic constants exhibit a change at this composition, this indicates that the elastic constants are sensitive to changes in the interactions of the



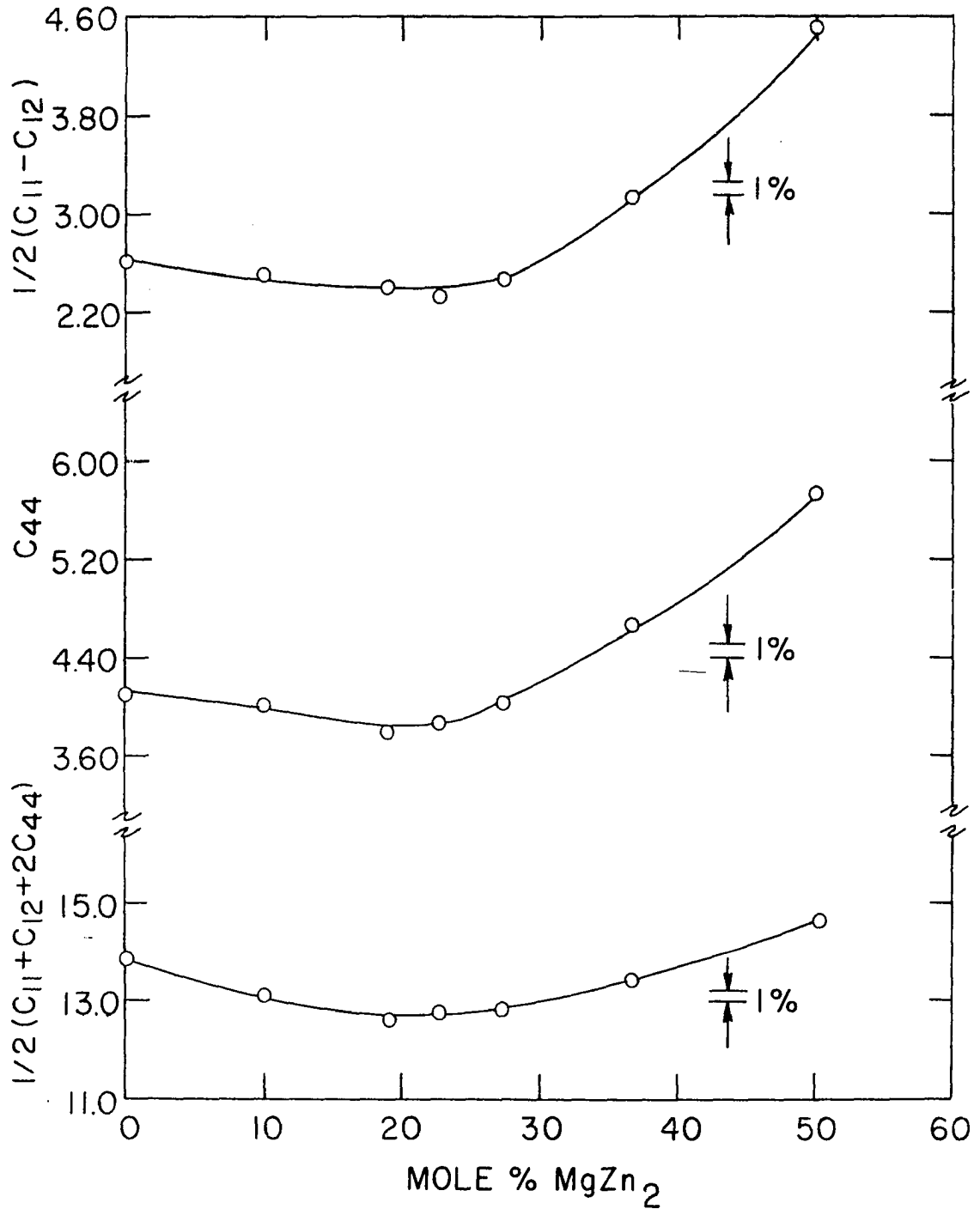


Figure 8. The room temperature compositional dependence of the elastic constants of the cubic Mg(Cu,Zn)<sub>2</sub> phases

Fermi surface with the Brillouin zones. In order to study this postulate further, the various energy contributions to the elastic constants have to be considered separately. As mentioned in the Introduction the elastic constants may be calculated if the energy of a crystal is known as a function of strain. For a volume conserving shear strain there are only three important energy contributions to the elastic shear constants (20). These are the electrostatic energy of an electrically neutral solid with a lattice of positive point charges embedded in a sea of uniform electron density, the repulsive exchange energy between ion cores, and the Fermi energy of the valence electrons. The elastic shear constants for copper, aluminum, and magnesium have been calculated by Fuchs (21), Leigh (22), and Reitz and Smith (23), respectively. Fuchs (21) extended Ewald's method of calculating the electrostatic energy of a lattice to obtain an expression relating the elastic shear constants to the real and reciprocal lattice vectors. To apply this type of calculation to a cubic Laves phase the lattice has to be considered as being composed of two sublattices. The space group of the unit cell is  $Fd\bar{3}m$  with the 16 B atoms at  $1/8, 1/8, 1/8, 1/8, 3/8, 3/8, 3/8, 1/8, 3/8, 3/8, 1/8$  plus the face-centering translations

and the 8 A atoms at 000, 1/4 1/4 1/4 plus the face-centering translations (3). Thus, the A atoms are in a diamond sublattice, and Wohlfarth (24) has calculated the electrostatic contribution of the elastic shear constants for the diamond lattice by Fuch's method with the following results:

$$C'(E) = -0.1544 \frac{Z^2 e^2}{2a} \quad (6)$$

and

$$C_{44}(E) = +0.2526 \frac{Z^2 e^2}{2a}, \quad (7)$$

where  $Z$  is the number of valence electrons per atom,  $e$  is the charge of an electron, and  $a$  is the lattice parameter.  $C'$  is defined in Equation 4 and  $(E)$  indicates the electrostatic contribution to the elastic constant. The A-A electrostatic bonding interactions may then be calculated from these relations. The relations needed for calculating the A-B and the B-B electrostatic bonding interactions were determined in the same manner as Fuchs with the following results:

$$C_{44}(E) = -1.0738 \frac{Z^2 e^2}{2a} \quad \text{for B-B bonds,}$$

$$C_{44}(E) = +4.4546 \frac{Z^2 e^2}{2a} \quad \text{for } \bar{A}\text{-B bonds,}$$

$$C'(E) = +1.9901 \frac{Z^2 e^2}{2a} \quad \text{for A-B bonds,}$$

$$C'(E) = +0.5002 \frac{Z^2 e^2}{2a} \quad \text{for B-B bonds,}$$

with the notation being identical to that in Equations 6 and 7. These equations represent the maximum contribution to the elastic constants. In a real metal the electron distribution is not necessarily uniform, and also the elastic distortion of the lattice will cause an additional modulation in the electron distribution. Both of these non-uniformities will lead to a reduction in the electrostatic contribution to the elastic constants (20). It may be noted that the A-B bonds are probably the dominate factors in the stability of these phases since the contribution of the A-B bonds to the elastic constants is much greater than the contribution of the A-A and B-B bonds.

The short-range repulsive energy due to the overlapping of closed shells may be calculated by assuming a Born and Mayer (25) type potential of the form

$$w(r) = Ab e^{(2r_c - r)/\rho} \quad (8)$$

where  $w(r)$  is the repulsive potential per ion pair,  $A$  is a constant that represents the dependence of the repulsive potential on the charge of the ions,  $r_c$  is the ion core radius, and  $r$  is the distance between ions. The constants  $b$  and  $\rho$  are determined from the lattice constants and compressibilities of ionic solids and are equal to  $10^{-12}$  ergs and  $0.33 \times 10^{-8}$  cm,

respectively, for most metals (20,25). The choice of the values of these constants in the present work is not critical since the core-core contributions to the elastic constants are small. A 50 per cent increase in  $\rho$  results in a change of less than 2 per cent in the elastic constant calculated from the electrostatic and core-core energy contributions. The doubling of  $b$  changes the above mentioned elastic constant by less than 0.3 per cent. The core-core repulsion contributions to the elastic constants (21) may then be expressed in the form

$$C'(I) = \frac{1}{2} \sum_r \frac{d^2 w}{dr^2} \left( \frac{dr}{d\epsilon_x} \right)^2 + \frac{dw}{dr} \frac{d^2 r}{d\epsilon_x^2}$$

and

$$C_{44}(I) = \sum_r \frac{d^2 w}{dr^2} \left( \frac{dr}{d\gamma_{xy}} \right)^2 + \frac{dw}{dr} \frac{d^2 r}{d\gamma_{xy}^2},$$

where  $w$  is defined in Equation (8),  $r$  is the distance between atoms, (I) indicates the core-core repulsion energy contributions to the elastic constant, and  $\epsilon_x$  and  $\gamma_{xy}$  are volume conserving shear strains corresponding to  $C'$  and  $C_{44}$ , respectively. The calculations of core-core energy contributions were based on the fact that each A atom has 12 nearest neighbor B bonds and 4 next-nearest neighbor A bonds. Each B atom has 6 nearest-neighbor B bonds. The effect of neighbors

beyond these is negligible. The results of this calculation and the electrostatic contribution calculation are given in Table 4. The data in Table 4 show that the electrostatic contribution alone is an order of magnitude larger than the measured elastic constants. This is partially due to the fact that a reduction factor that can vary from 0 to 1 has to be applied to the electrostatic calculation to compensate for electronic shielding (18). The choice of a screening factor of approximately 0.6 will bring the values of the calculated and measured elastic constants into better agreement. Also, since the major energy contribution to the elastic constants appears to be the electrostatic energy term, then the calculation of the anisotropy ratio,  $2C_{44}/(C_{11}-C_{12})$ , will tend to minimize the effect of the screening factor. Figure 9 shows that the calculated anisotropy ratios are in close agreement with the measured values. However, there is a maximum in the measured anisotropy ratio at approximately 20 mole per cent  $MgZn_2$  which is the point at which Fermi energy contributions would be expected to be important. Also the measured anisotropy ratios show a stronger compositional dependence than the calculated values. Thus, it appears that the Fermi energy terms are needed to achieve better agreement between the cal-

Table 4. Calculated and observed values of the cubic elastic constant in units of  $10^{12}$  dynes/cm<sup>2</sup>

Mole %	Max. C <sub>44</sub> (E)	C <sub>44</sub> (I)	Total C <sub>44</sub>	Obs. C <sub>44</sub> at 0°K	Max. C'(E)	C'(I)	Total C'	Obs. C' at 0°K
0	.718	.070	.788	.425	.379	.048	.427	.267
9.99	.717	.069	.786	.414	.408	.047	.455	.260
19.00	.721	.068	.789	.400	.435	.047	.482	.247
22.63	.721	.067	.788	.419	.446	.046	.492	.243
27.34	.726	.067	.793	.428	.463	.045	.508	.262
36.70	.728	.066	.794	.490	.494	.043	.537	.345
50.11	.736	.064	.800	.629	.545	.041	.586	.471

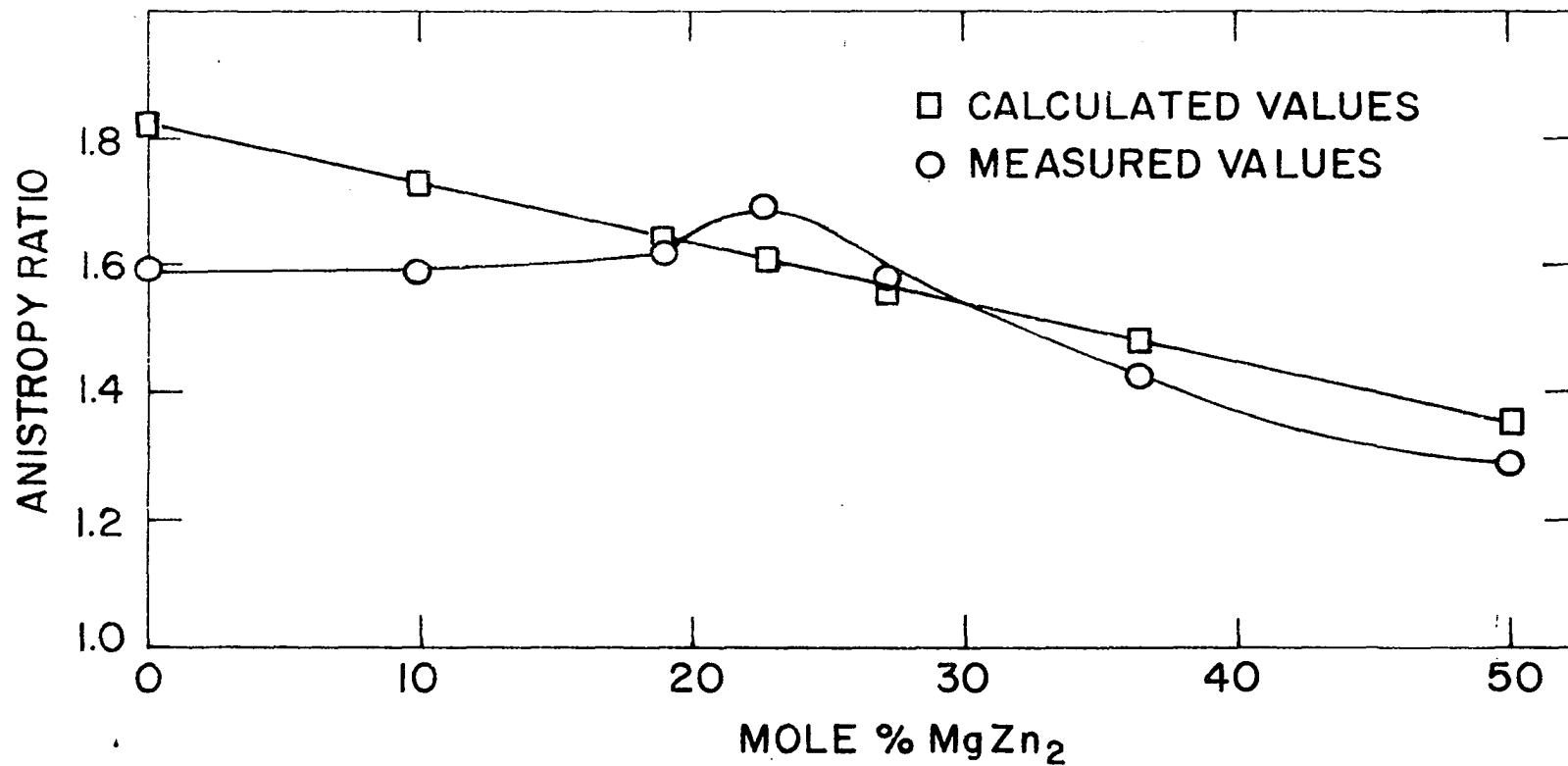


Figure 9. The calculated and measured values of the anisotropy ratio for the cubic Mg(Cu,Zn)<sub>2</sub> phases



culated and measured elastic constants. However, since little or no information is available on the shape of the Fermi surface of Laves phases, it is practically impossible to calculate the Fermi energy contributions.

### The Debye Temperature

The Debye theory of specific heat is a useful theory because it can describe the vibrational properties of a crystal lattice with a single parameter. Also this parameter need not be determined only from specific heat measurements, but may also be determined from elastic constant data. The principal difficulty in calculating the Debye temperature from the elastic constants is in finding the average value of a function of the three roots of a cubic equation. Reference may be made to the recent review article by Alers (26) for more details on the difficulties in determining the Debye temperatures from the elastic constants. A simplified method has been proposed by de Launay (27) that is completely adequate for materials that are nearly elastically isotropic. Since the maximum anisotropy ratio of the cubic  $\text{Mg}(\text{Cu},\text{Zn})_2$  alloys is 1.83, this is the method employed in the present investigation. The model suggested by de Launay considers

the lattice to be of the Born-von Karman type with central forces connecting nearest and next-nearest neighbors and includes the contribution of the free electron gas. This model only considers the acoustic vibrational modes but at very low temperatures there is insufficient energy to excite the optical modes. Wolcott (28) has developed a method, which is similar to that of de Launay, for determining the Debye temperature for a hexagonal crystal from the single crystalline elastic constants. The Debye temperature of  $\text{MgZn}_2$  was calculated by this method.

Steiner (29) has measured the specific heats of several of the cubic  $\text{Mg}(\text{Cu},\text{Zn})_2$  Laves phases in the temperature range  $1.4^\circ\text{K}$  to  $5^\circ\text{K}$  and fitted the data to a  $C_p/t$  vs  $T^2$  plot. She then calculated the Debye temperatures from these plots and the results are given in Table 5 along with the values determined in this investigation. The results agree satisfactorily up to about 20 mole %  $\text{MgZn}_2$ , at which point the Debye temperatures determined from elastic constants are larger than the Debye temperatures determined from specific heat measurements, with the magnitude of this difference increasing with increasing zinc content. The exact cause of this discrepancy is not known. It is unfortunate that Steiner's results were given

in a short note that did not state all of the details of the sample preparation and measurements.

Table 5. The Debye temperatures of  $\text{Mg}(\text{Cu},\text{Zn})_2$  alloys

Composition mole% $\text{MgZn}_2$	Specific heat $\theta_D$ ( $^\circ\text{K}$ )	Composition mole% $\text{MgZn}_2$	Elastic constant $\theta_D$ ( $^\circ\text{K}$ )
0	332.5	0	336.4
10	327.6	9.99	331.5
20	318.5	19.00	326.3
30	311.0	22.63	330.5
40	314.4	27.34	336.5
50	309.8	36.70	369.8
60	308.0	50.11	422.7
		100	329.9

If the interatomic force constants are assumed to be independent of composition, then the treatment of Kittel (9) may be extended to show that for a polyatomic lattice the Debye temperatures are inversely proportional to the square root of the mass of the atoms per formula weight. Therefore, in the quasi-binary  $\text{MgCu}_2$ - $\text{MgZn}_2$  system the replacement of copper atoms by zinc atoms should cause a monotonic decrease in the Debye temperature. This is the case at low zinc contents. However, at compositions above 20 mole per cent  $\text{MgZn}_2$  the Debye temperatures determined from the elastic constants increase implying that the assumption of the invariance of

the interatomic force constants is invalid. This is not surprising since the elastic constants are the resultant of all force constants in a crystal and the elastic constants increase at compositions above 20 mole per cent  $\text{MgZn}_2$ .

#### Bulk Modulus of the Electron Gas

The de Launay model of a crystal lattice also implies that the bulk modulus of the electron gas,  $K_e$ , is equal to  $C_{12} - C_{44}$ . This term is simply the discrepancy in the Cauchy relation and this result seems reasonable since Fuchs (21) has attributed the failure of the Cauchy relation in metals to the presence of the conduction electrons. For metals the bulk modulus of the electron gas is generally a positive quantity, but the alloys measured in this investigation show that at room temperature  $K_e$  becomes negative at approximately 42 mole per cent  $\text{MgZn}_2$  as shown in Figure 10. Also Figure 2 shows that the magnetic susceptibility changes from paramagnetic to diamagnetic at approximately 48 mole per cent  $\text{MgZn}_2$ . Both of these values were determined from smoothed curve values, and it is possible that the true values may even be in closer agreement. Materials that are known to have large covalent contributions to their binding energy, such as the diamond form of carbon, silicon, germanium, and  $\text{ZnS}$ , also have

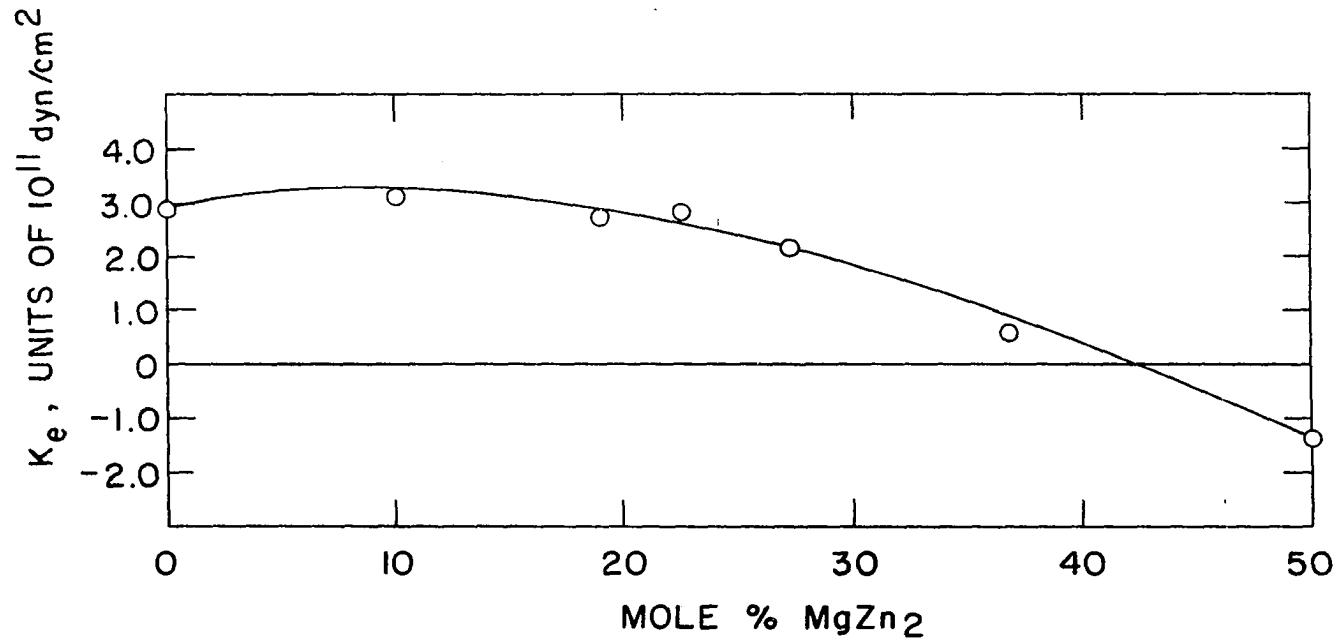


Figure 10. The bulk modulus of the electron gas for the cubic  $Mg(Cu,Zn)_2$  phases

negative electron gas bulk moduli (20). Since materials that are covalently bonded generally have diamagnetic susceptibilities, this is an indication that there may be a certain amount of covalent bonding interactions in these cubic Laves phases. It is possible that the agreement is fortuitous but this is unlikely since  $K_e$  becomes negative and the susceptibility becomes diamagnetic at nearly the same composition.

## SUMMARY

The compositional dependence of the single crystalline elastic constants of the cubic  $\text{Mg}(\text{Cu},\text{Zn})_2$  Laves phases were found to exhibit a minimum at approximately 20 mole per cent  $\text{MgZn}_2$  and the anisotropy ratio showed a maximum at this same composition. These extrema are probably related to Fermi surface interactions with the Brillouin zones. It was also concluded that the Fermi energy terms are necessary to calculate the elastic constants and their compositional dependence.

The Debye temperatures of the cubic  $\text{Mg}(\text{Cu},\text{Zn})_2$  Laves phases were found to first decrease and then increase with increasing zinc content. The initial decrease may be due to the substitution of the heavier zinc atoms for copper atoms while the increase in Debye temperatures above 20 mole per cent  $\text{MgZn}_2$  is probably due to an increase in the interatomic force constants.

It was also found that the bulk modulus of alloys in the  $\text{MgCu}_2$ - $\text{MgZn}_2$  system follow a linear relationship. This provides further validation for the arithmetic mean approximation.

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