Title

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Thermal Expansion and Elastic Constants of β′-AgMg. II. Single-Crystal Elastic Constants from 77° to 750°K

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The single-crystal adiabatic elastic constants of stoichiometric β'-AgMg have been determined from 77° to 750°K using the ultrasonic pulse-echo technique. The values obtained at 300°K are: $c_{11}=0.8380$, $c_{12}=0.5635$, $c_{44}=0.4755$ (all in units of 10^{12} dyn/cm^2).

A relationship between the elastic constants and the lattice parameters of the two β'-structures AgMg and CuZn was found. A similarity of the temperature dependence of the elastic constants was also observed. From the extrapolated values of the elastic constants at 0°K, a Debye temperature of 287°K was obtained. Finally, using the elastic constant data, specific heat of β'-AgMg at constant volume was calculated and found to compare favorably with the classical value $3R$ at high temperature.

INTRODUCTION

RECENTLY the elastic constants of the intermetallic compound β'-CuZn have been redetermined by McManus[1] over the temperature interval, 4.2°–800°K utilizing the ultrasonic pulse-echo technique. In contrast to previous findings,[2] McManus found the shear anisotropy ratio $A=C/C'=5.4$ at 0°K instead of the anomalously large value of 18.7. Moreover, the shear constant C' was found to decrease with temperature rather than increase. However, it is noteworthy to point out that over the temperature interval 0°–500°K, C' for β'-CuZn decreases only about 2% while c_{11} and c_{44} decrease about 11% and 18%, respectively. In view of the structural similarity between β'-CuZn and β'-AgMg, it was felt desirable to measure the elastic constants of β'-AgMg, as a contribution to a better understanding of intermetallic compounds.

In the present study, the elastic constants C_{11}', C, and C' of β'-AgMg were determined from 77° to 750°K by means of the ultrasonic pulse-echo technique. From the elastic constants, the Debye temperature was calculated and available specific-heat data at high temperatures were analyzed in terms of the various contributions.

EXPERIMENTAL PROCEDURE

The three elastic constants $C_{11}'=\frac{1}{2}(c_{11}+c_{12}+2c_{44})$, $C=c_{44}$ and $C'=\frac{1}{2}(c_{11}-c_{12})$ were obtained by measuring the velocities of plane longitudinal waves and appropriately polarized transverse waves propagating in the ⟨110⟩ direction. The velocities of the ultrasonic waves were measured by means of a Sperry Products ultrasonic attenuation comparator. The longitudinal and transverse waves were generated, respectively, by $\frac{1}{2}$-in.-diam 10-Mc/sec X-cut and Y-cut quartz crystals, which were bonded to the specimen by Fisher nonaqueous stopcock grease at low temperatures and by a

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[1] G. M. McManus, Phys. Rev. 129, 2004 (1963).

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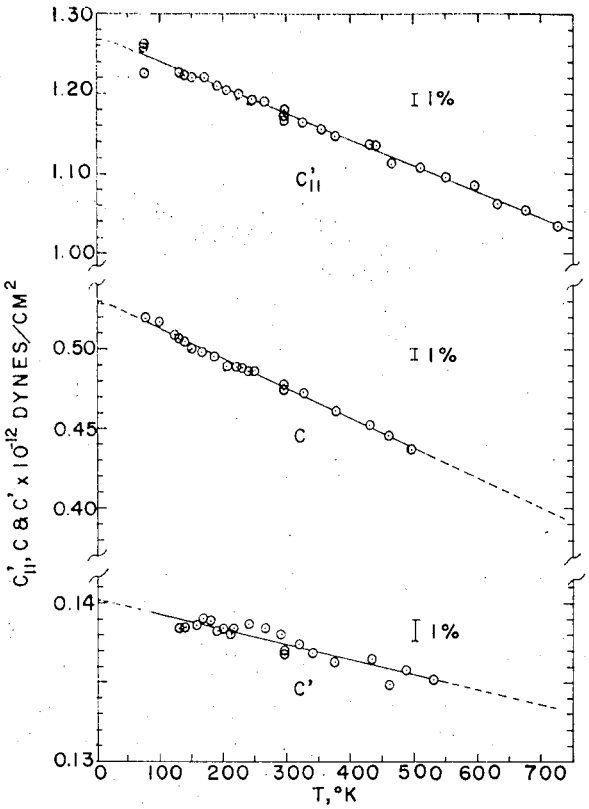

FIG. 1. The adiabatic elastic constants of β'-AgMg as a function of temperature.

special epoxy resin at high temperatures. The details regarding the application of this epoxy resin and the experimental apparatus have been described before.[3,4]

The β'-AgMg single crystal, which was kindly supplied by Dr. H. A. Domian, formerly of the Ford Scientific Laboratory, was grown in an inert atmosphere using a modified Bridgman technique. The composition was determined to be 50.0±0.5 at. % Mg by microprobe analysis. Specimens with faces normal to the ⟨110⟩ direction were cut from the single crystal by electric discharge machining. The orientation of these surfaces was within 0.5 deg of the ⟨110⟩ direction as determined by means of the back reflection Laue method. The two ⟨110⟩ faces were lapped to be flat and parallel with each other to within ±0.0002 cm in a manner described previously.[4]

The room temperature density $\rho=6.033$ g/cm^3, used in computing the elastic constants of the β'-AgMg alloy at 50.0±0.5 at. % Mg, was calculated from the lattice parameter $a=3.3135$ Å, reported by Ageev and Kuznetzov,[5] and Hagel and Westbrook.[6]

The variation of density and specimen dimensions with temperature was taken into account using the thermal expansion data reported in part I of the present work.[7]

RESULTS

The three directly measured elastic constants, $C_{11}'=\rho v_t^2$, $C=\rho v_{l_1}^2$, $C'=\rho v_{t_2}^2$, are plotted as a function of temperature in Fig. 1. The term v_l is the plane logitudinal wave velocity, and v_{t_1} and v_{t_2} are the velocities of transverse waves with particle motions in the ⟨100⟩ and ⟨110⟩ directions respectively, all propagating in the ⟨110⟩ direction. Within the scatter of the data, all three quantities C_{11}, C, and C' decrease linearly with temperature, and the solid lines shown in Fig. 1 were obtained by means of a least-square fit of the experimental data.

In the absence of measurements at liquid helium temperatures, the values of C_{11}', C, and C' were extrapolated to 0°K with zero slopes at 0°K. The extrapolations in this region, represented by the dashed curves, were made so that the data would be internally consistent at absolute zero. At high temperatures, it was possible to measure only the values of v_l up to about 750°K. For v_{t_1} and v_{t_2}, in spite of repeated tries, the epoxy resin which served as the bonding agent between the specimen and the quartz transducer failed as a good acoustic medium. Similar difficulties were also encountered in the case of determining the velocities of ultrasonic waves for Ag and Au using the same bonding agent.[4] However, in view of the linear temperature dependence of C_{11}', C, and C' up to 500°K and the fact that β'-AgMg is ordered at higher temperatures it seemed justifiable to extrapolate the values of C and C' linearly to 750°K, the highest temperature at which C_{11}' was measured.

From Fig. 1, the smoothed values of C_{11}', C, and C' as well as the derived elastic constants c_{11} and c_{12} were obtained. They are summarized in Table I together with the calculated values of the adiabatic bulk modulus, $B_s=\frac{1}{3}(c_{11}+2c_{12})=C_{11}'-C-\frac{1}{3}C'$, the isothermal compressibility,[8] $\chi_T=(1/B_s)+(9\beta^2TV/C_p)$, (where β is the linear coefficient of thermal expansion, T the absolute temperature, V the specific volume, and C_p the specific heat at constant pressure) and the shear anisotropy, $A=C/C'$. The extrapolated values at 0°K and at high temperatures are listed in parenthesis to distinguish them from the experimentally measured values.

The number of the significant figures shown in Table I is greater than is warranted by the absolute accuracy of the measurements, but an extra figure has been retained to indicate the trend of the data with tempera-

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[8] For example: N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

TABLE I. Elastic properties of β'-AgMg. The adiabatic elastic constants are in units of 10^{12} dyn/cm^2; the shear anisotropy ratio $A=C/C'$ is dimensionless and the isothermal compressibilities are in units of 10^{-13} cm^2/dyn.

T (°K)	C_{11}'	C'	$C=c_{44}$	c_{11}	c_{12}	B_s	A	χ_T
0	(1.27)	(0.140)	(0.529)	(0.881)	(0.601)	(0.695)	(3.78)	(14.4)
77	1.250	(0.1395)	0.5170	0.8720	0.5930	0.686	3.71	14.7
100	1.240	0.1395	0.5125	0.8685	0.5900	0.683	3.68	14.8
150	1.225	0.1390	0.5035	0.8610	0.5835	0.676	3.63	15.1
200	1.210	0.1385	0.4940	0.8535	0.5765	0.669	3.57	15.3
250	1.190	0.1380	0.4845	0.8455	0.5700	0.662	3.52	15.6
300	1.175	0.1375	0.4755	0.8380	0.5635	0.655	3.46	15.8
350	1.160	0.1370	0.4660	0.8304	0.5565	0.648	3.40	16.1
400	1.145	0.1365	0.4565	0.8230	0.5500	0.641	3.35	16.4
450	1.125	0.1360	0.4475	0.8150	0.5435	0.634	3.29	16.7
500	1.110	0.1355	0.4380	0.8075	0.5365	0.627	3.23	17.0
550	1.095	1.1350	0.4285	0.8000	0.5300	0.620	3.18	17.3
600	1.075	(0.1345)	(0.4195)	(0.7925)	(0.5235)	(0.613)	(3.12)	(17.6)
650	1.060	(0.1340)	(0.4100)	(0.7845)	(0.5165)	(0.606)	(3.06)	(17.9)
700	1.045	(0.1335)	(0.4005)	(0.7770)	(0.5100)	(0.599)	(3.00)	(18.2)
750	1.030	(0.1330)	(0.3915)	(0.7695)	(0.5035)	(0.592)	(2.94)	(18.6)

ture. Based on the scatter of the experimental data from the least-square values, the standard deviations in the directly measured quantities C_{11}', C, and C' are found to be $\pm 0.5\%$. Using the standard propagation-of-error treatment,[9] the corresponding standard deviations in the derived quantities c_{11}, c_{12}, and B_s are $\pm 0.7\%$, $\pm 0.9\%$, and $\pm 0.9\%$, respectively.

DISCUSSION

Except for data of the electrical resistivity of AgMg[10,11] no other electronic properties have been measured and a rigid theoretical calculation of the elastic constants is not possible. Calculations for β'-CuZn by McManus[1] based on Coulomb forces only, showed a considerable discrepancy between the calculated and the measured elastic constants.

However, an interesting comparison can be made between the measured elastic constants of β'-AgMg and β'-CuZn. For a lattice of ions of the same valency and the same repulsive forces, one would expect the elastic constants to be proportional to $1/a^4$, where a is the lattice parameter at 0°K. It is surprising that this relationship holds true extremely well for at least two of the elastic constants of β'-AgMg and β'-CuZn, as shown in Table II.

TABLE II. Relationship between elastic constants and lattice parameters.

	β'-AgMg	β'-CuZn	β'-NiAl[a]
a (Å)	3.298	2.95	2.88
$c_{11}\times 10^{-12}$ (dyn/cm^2)	0.881	1.40	2.11
$c_{12}\times 10^{-12}$ (dyn/cm^2)	0.601	1.096	1.43
$c_{44}\times 10^{-12}$ (dyn/cm^2)	0.529	0.823	1.12
$c_{11}\times a^4$	105	106	146
$c_{12}\times a^4$	71	83	99
$c_{44}\times a^4$	63	62	77

[a] The values of NiAl are for room temperature.

The elastic constants at 0°K were taken for β'-AgMg from the present work, and for β'-CuZn from McManus.[1] The values of the lattice parameters are for the stoichiometric compounds at 0°K. The table includes values of β'-NiAl,[12] which has the same CsCl structure. This intermetallic compound shows considerably less agreement, probably not because room-temperature values had to be taken, but because of the different charges of the "ions." The same relationship was discovered earlier for compounds with the diamond structure by Keyes.[13]

Another resemblence between β'-AgMg and β'-CuZn is the temperature dependence of their elastic constants. Over the temperature interval, 0°–500°K, c_{11}, c_{44}, and $C'=\frac{1}{2}(c_{11}-c_{12})$ of β'-CuZn decrease about 11%, 18%, and 2% respectively.[1] Within the same temperature interval, c_{11}, c_{44}, and C' of β'-AgMg decrease about 8%, 17%, and 3%. In order to account for the temperature dependence of the two shear constants for β'-CuZn, McManus had to consider the second-neighbor term in the non-Coulombic contribution to the elastic constants. The nearest-neighbor term along would have resulted in an increase in the shear elastic constant C' with temperature. The qualitative explanation can be applied to the β'-AgMg data also.

For β'-NiAl, Wasilewski[12] measured the room temperature values of c_{11}, c_{44}, $\frac{1}{2}(c_{11}-c_{12})$, and the temperature dependence of the Young's moduli E_{100} and E_{111}. These data do not permit an exact derivation

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[13] R. W. Keyes, J. Appl. Phys. **33**, 3371 (1962).

of the temperature dependence of C and C'. However, from the relationships between the Young's moduli and the elastic constants for cubic crystals

$$E_{100}=3CC'/[C+(C'/3B_s)] \quad (1)$$

$$E_{111}=3CC'/[C+(C/3B_s)] \quad (2)$$

one can draw some qualitative conclusions regarding the temperature dependence of C and C'. Wasilewski's data show that in the temperature interval 150°–650°K, E_{111} decreases about 13% while E_{100} decreases only 7%. Since the major contribution to E_{100} and E_{111} according to Eqs. (1) and (2) are C' and C, respectively, one may conclude that C' has a smaller temperature dependence than C.

Wasilewski's data yield a shear anisotropy ratio $A=3.3$ at room temperature, while the corresponding values for β'-CuZn and β'-AgMg obtained by McManus and the present authors are 4.9 and 3.5. These data definitely suggest that the shear anistropy ratio for the CsCl type of intermetallic compounds, that have been determined so far, is not abnormally large as earlier elastic constant data of β'-brass[2] suggested.

In addition, the elastic constants were used to evaluate the Debye temperature and the lattice specific heat. Using the method suggested by Anderson[14] for averaging the elastic constants, a value of $\theta_D=287°\pm3°$K was obtained at 0°K. Since specific heat data are not available at low temperatures no comparison between the values of θ_D obtained by thermal and elastic properties was made.

Finally the specific heat at constant volume C_v was evaluated from 150° to 750°K by subtracting the dilational specific heat from the experimentally determined specific heat at constant pressure C_p. The values of the coefficient of thermal expansion and the specific volume were taken from the literature[5–7] and those of the isothermal compressibility were obtained in the present study in order to calculate the values of the dilational specific heat. Using the C_p data reported by Schübel[15] and Schimpff[16] over the temperature interval 100°–900°K, the values of C_v so obtained approach the classical value of $3R=5.96$ cal/deg·g-atom at high temperatures within the uncertainties of the experimental quantities.

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