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by Y. Austin Chang* and Ralph Hultgren**.

INTRODUCTION

Heat capacities of solids and liquids are always measured at constant pressure, Cp, while theoretical treatments apply to Cv, the heat capacity at constant volume. The difference, Cp - Cv, is called the dilation contribution. Strictly speaking, $Cp - Cv_o$, where v_o is the volume at 0°K, is desired. However, at temperatures of interest this term cannot be evaluated for most substances because the pressures necessary to compress the volume to v_o are much too high to be experimentally attainable.

For v, the volume at the temperature in question, the dilation term for cubic materials is

$$C_{dil} = Cp - Cv = 9\,\alpha^2 VT/K_T \tag{1}$$

where α is the linear coefficient of thermal expansion, V is the volume, T is the temperature, and K_T is the isothermal compressibility.

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The compressibility has been measured for relatively few substances, mainly at room temperature only. Data for alloys are almost nonexistent, and very few pure metals have been measured above room temperature. Thus, the dependence of the dilation term on temperature is inadequately established and the dependence on alloy composition is not known.

This affects our understanding of heat capacity, particularly the approximate prediction of heat capacity at high temperatures for engineering purposes. The most practical approach to this problem at present is an empirical one. The total measured heat capacity is assumed to be made up of the sum of several independent terms, such as harmonic lattice vibration (Debye term), dilation, electronic contributions, and second order transitions in the metal or alloy, such as magnetic and order-disorder changes.

At low temperatures, the dilation term is too small to be significant for such an empirical study; it tends to zero at 0°K. However, its importance increases with temperature. It may constitute as much as 3 to 8 percent of the total Cp at room temperature and much more at elevated temperatures. Thus, the dilation term is most important in the temperature region in which it is least known.

The present work was planned to improve knowledge of the temperature and composition dependence of the dilation term. By means of the ultrasonic pulse-echo technique, compressibilities of copper and an alpha-brass with 9.7 atom percent zinc were measured from 77°-800°K. Measurements were also made of alpha-brasses of of higher zinc contents. Because of increased attenuation, the echoes were not good enough for quantitative results; they will be mentioned only qualitatively. Heat contents of the alpha-brass were also measured at high temperatures.

The dilation contribution was calculated as a function of temperature and composition. The validity of the Nernst-Lindemann relationship was tested from these and other results found in the literature.

MATERIALS AND SPECIMEN

A cast ingot of OFHC grade copper was cold-rolled and machined to a cylinder of 5/8-inch diameter by 1/2-inch long. The two faces of the specimen were ground and polished parallel to ± 0.0002 inches. The specimen was then annealed at 400°C for one hour to obtain an average grain diameter of 0.015 mm. Spectroscopic analysis indicated traces of impurities in weight percent: Ag, 0.003, and Ni, 0.003. The lattice constant of the speciment was 3.6152 Å in comparison to 3.6148 Å given in Pearson's Handbook.[1]

The brass specimen in the form of 3/4-inch rod was kindly supplied by Bridgeport Brass Company, which furnished the following analysis in weight percent: Cu, 90.05, Zn, 9.93, Bi, 0.001, Fe, 0.005, Ni, 0.01, Pb, 0.003, and Sn, 0.00. A specimen 1/2-inch thick was machined from this rod, surface-ground and polished, annealed at 450°C for one and a half hours and microscopically examined. The average grain diameter was 0.025 mm. Filings were also taken from the same rod and strain annealed at 450°C. Sharp peaks on the back-reflection CuKα X-ray diffraction pattern indicated homogeneity of the alloy. The lattice constant of 3.6355 Å agrees with that given by Pearson[1] for the zinc concentration of 9.7 atom percent shown by the chemical analysis.

EXPERIMENTAL METHOD

Ultrasonic Velocity Measurement

The velocities of ultrasonic waves in copper and alpha-brass with 9.7 atom percent of zinc were measured by means of a Sperry Ultrasonic Attenuation Comparator, Style 56A001, together with a low frequency receiver, PR 603. 10 Mc X-cut and Y-cut quartz crystals of 1/2-inch diameter were used to generate respectively pure longitudinal or shear waves. When the quartz crystal is suitably bonded to the test specimen, the ultrasonic waves generated by the transducer pass through the specimen and set up a series of echoes within the material. From these echoes displayed on a built-in oscilloscope, the round-trip time of each echo was measured. Knowing the specimen length, the velocity may be calculated.

From the longitudinal and transverse velocities, the adiabatic compressibility

$$K_S = \frac{1}{\rho(v_\ell^2 - \frac{4}{3} v_t^2)} \qquad (2)$$

where ρ is the density, v_ℓ the longitudinal velocity, and v_t the transverse velocity. The isothermal compressibility, K_T, can be found from K_S by the following equation:

$$K_T = K_S + \frac{9\alpha^2 TV}{C_p} \qquad (3)$$

The principal experimental difficulty in this study was finding a material which would firmly bond the transducer to the specimen. At low temperatures, Fisher non-aqueous stopcock grease served very well. However, all bonding materials tried, including Sauereisen cement P-31, Biggs epoxy resin R-385, and a mixture of Na_2SiF_6, $BaSO_4$, and Na_2SiO_4, failed as the temperature was raised. The best material proved to be an epoxy resin which was a mixture of Epon 1031 and nadic methyl anhydride, catalyzed by benzene dimethyl amine added at about 50° C. The formula and material were kindly supplied by Dr. Harold Chen of the Shell Development Co., Emeryville, California. This bond was excellent up to about 500° K. Above this temperature, it lost its acoustic strength, as evidenced by a sudden drop of the echo intensity. However, the signals were strong enough to permit measurements to 800° K. On cooling the specimens, the bond broke. Black powder found between the specimen and quartz crystal was believed to be carbon from decomposition of the epoxy resin.

The experimental arrangement is shown in Figure 1. For low temperature measurements, the system was evacuated and immersed in a liquid nitrogen bath; the rate of cooling was adjusted by changing the level of liquid nitrogen in the dewar. Measurements were completed so rapidly that they could be made during cooling. Elevated temperatures were obtained by use of a glass heating tape wrapped around the Pyrex tube in place of the dewar; the whole was insulated by Kaylo insulating material. Temperatures were measured by means of a 30-gauge copper-constantan thermocouple inserted in the thermocouple well, in the stainless steel plate at the bottom.

Heat Content Measurement

The heat contents above room temperature of alpha-brass with 9.7 atom percent zinc were determined in a diphenyl ether drop calorimeter described elsewhere.[2,3] The alloy heated to a temperature T was dropped into a chamber surrounded by a second chamber containing liquid and solid diphenyl ether at its melting point, 300°K. The heat given off by the sample melts some of the solid without changing its temperature. The resulting expansion of the diphenyl ether forces mercury out a capillary tube. The amount of heat given off is proportional to the volume of mercury displaced.

RESULTS AND DISCUSSION

Ultrasonic Velocity and Compressibility

The measured longitudinal and transverse velocities are shown in Figures 2 and 3. The scatter of data at all temperatures is less than the stated accuracy (±1%) of the Sperry instrument. This corresponds to a somewhat larger (±3%) scatter in the compressibilities calculated from them. Corrections for changing length of samples with temperature were calculated from thermal expansion data 4, 5, 6, 7 interpolating for zinc content where necessary and using the fact that the coefficient of thermal expansion is approximately proportional to the heat capacity. Measured compressibilities at 300° K agree with those found in the literature (Table I).

TABLE I. Comparison of Compressibilities at 300° K

Investigation	Copper	α-Brass
This study	7.20×10^{-13}	7.77×10^{-13}
*Schmunk and Smith[8]	7.18×10^{-13}	
*Overton and Jaffney[9]	7.29×10^{-13}	
*Lazarus, 298°K[10]	7.17×10^{-13}	
*Rayne[11]	7.30×10^{-13}	7.80×10^{-13}
*Chang and Himmel[12]	7.25×10^{-13}	
**Bridgman[13]	7.12×10^{-13}	

* Single crystal, ultrasonic measurement. Measurements of Chang and Himmel also confirm the temperature dependence of compressibility found in this work.

** Polycrystal, static technique

As shown in Table II, the compressibility increases with temperature and zinc content. Other measurements were made on brasses with higher zinc contents. Because of high attenuation of the echoes these measurements were not so precise and have not been tabulated. They show clearly, however, that compressibility increases with zinc content.[14] The data required to convert the experimental adiabatic compressibilities, K_S, to the isothermal compressibilities, K_T, by equation (3), were found in the literature.[1, 4-7, 15]

TABLE II. Measured Compressibilities

T, °K	Compressibility (cm^2/dyne) x 10^{13}			
	K_S		K_T	
	Copper	Brass, x_{Zn} = 0.097	Copper	Brass, x_{Zn} = 0.097
77	6.96	7.53	7.00	7.56
100	6.99	7.55	7.03	7.59
200	7.09	7.65	7.21	7.79
298.15	7.20	7.77	7.42	8.00
400	7.32	7.89	7.63	8.23
500	7.48	8.04	7.88	8.48
600	7.67	8.20	8.18	8.76
700	7.87	8.37	8.50	9.07
800	8.10	8.86		

Heat Content

Because the high temperature heat capacities of brass measured by Kussmann and Wollenberger[16] disagreed with low temperature values of Huffstutler[17] by about 0.45 cal/g atom deg at room temperature, it was decided to repeat the work and extend it to higher temperatures by heat content measurements. The results, shown in Table III, have been adopted for this work. Derived Cp values are shown in Table IV. They extrapolate to Cp = 5.84 at 298.15° K, agreeing with Huffstutler's determination. For copper, Cp values were taken from the literature.[15]

TABLE III. Experimental Heat Contents of Alpha-Brass

T, ° K	$H_T - H_{st}$	T, ° K	$H_T - H_{st}$	T, ° K	$H_T - H_{st}$
373.8	441	637.9	2079	656.5	2237
404.0	636	699.5	2481	606.5	1872
451.9	915	752.1	2704	551.9	1551
497.0	1203	806.3	3189	488.8	1156
564.9	1626	808.0	3130	447.2	897
611.2	1900	756.2	2847	405.8	636
611.6	1922	697.1	2441	345.2	282

TABLE IV. Heat Capacities and Dilation Term

	Copper			Alpha-Brass		
T, ° K	Cp	Cp-Cv	$A \times 10^5$	Cp	Cp-Cv	$A \times 10^5$
77	2.98	0.02	2.21	3.05	0.01	1.58
100	3.84	0.02	1.68	3.95	0.03	1.68
200	5.41	0.10	1.68	5.42	0.10	1.68
298.15	5.84	0.17	1.68	5.84	0.17	1.68
400	6.04	0.24	1.68	6.06	0.25	1.68
500	6.19	0.32	1.68	6.21	0.32	1.68
600	6.34	0.40	1.64	6.33	0.40	1.68
700	6.48	0.48	1.64	6.42	0.49	1.72
800	6.62	0.57	1.63			

Dilation Contribution

Values of the dilation contribution (Table IV) $C_{dil} = Cp - Cv$, were calculated from equation (1), using measured values of the compressibility (Table II) and other quantities from the literature.[1, 4-7]

The resulting dilation terms were then used to test the validity of the Nernst-Lindemann semi-empirical equation. This equation, derived with the aid of certain considerations of Grüneisen, has been frequently used to estimate the dependence with T of C_{dil} at elevated temperatures, though it has been inadequately tested above room temperature. According to the equation

$$C_{dil} = ACp^2T$$

where A ($=9\alpha^2V/Cp^2K_T$) is assumed constant with temperature. As can be seen in Table IV, A is satisfactorily constant except at 77°K for both copper and alpha brass.

The applicability of the Nernst-Lindemann equation was tested for five additional metals and three nonmetallic substances for which sufficient data was found in the literature (see Table VI). For each of these a constant, A, was chosen which fitted the data exactly at 300°K. For a rather high temperature in each case, the experimental C_{dil} was compared with the calculated as shown in Table V. Evidently the equation tends to overestimate the dilational contribution; copper and brass are the most favorable of all the substances. However, in spite of the considerable overestimate, the magnitude of the error seldom exceeds 0.2 cal/deg g-atom, and is usually of the order of 0.1.

The experimental values of the heat capacity, Cp, were satisfactorily accounted for at all temperatures as the sum of a lattice vibrational (Debye) term, C_D, the dilation term, and an electronic contribution term, C_{el}.

$$Cp = C_D + C_{dil} + C_{el}$$

The excellent agreement for copper is shown in Fig. 4; the agreement for brass was as good. In these calculations the Debye temperatures were taken as 315°K and 308°K for copper and brass, respectively. For the electronic terms, it was assumed that $C_{el} = \gamma T$, and that the value of γ found at very low temperatures applied at high temperatures. For copper, $\gamma = 1.64 \times 10^{-4}$, was taken from the literature;[15] for brass, the value $\gamma = 1.78 \times 10^{-4}$ was taken from Rayne.[18]

TABLE V. Dilational Heat Capacities

Substance	Temperature, °K	C_{dil}, cal/g atom deg K		
		Experimental	Calculated	Deviation %
Cu	800	0.57	0.59	+3.5
Brass, 9.7 at % Zn	750	0.53	0.52	-1.9
Zn	650	0.72	0.86	+19.4
In	400	0.75	0.79	+5.3
Al	800	0.90	1.15	+27.8
Pb	600	0.87	1.22	+40.2
Sn	500	0.53	0.62	+17.0
KCl	1000	1.34	1.44	+7.5
NaCl	700	0.92	1.03	+12.0
MgO	1400	0.49	0.59	+20.4

TABLE VI. References Used as Data Source

Material	K_S	K_T	Cp	α	ρ
Zn	19		15	20	1
Al	21		15	4	1
In		22	22	23	1
Sn		22	22	24	1
Pb		22	22	4	1
KCl	25, 26		29	30, 31	32
NaCl	27, 35		29	33	32
MgO	28		29	34	32

Summary and Conclusions

The compressibility as a function of temperature has been measured for copper and brass (9.7 at. percent zinc) from sonic velocities. With the aid of these data the dilational contribution to the heat capacity, Cp-Cv, has been calculated from 77° K to 800° K. This term amounts to less than 3 percent of the total heat capacity at room temperature and below, but becomes much more important at elevated temperatures.

The Nernst-Lindemann empirical equation satisfactorily predicts the dilational term for copper and the brass. For other substances, it gives a result considerably too high.

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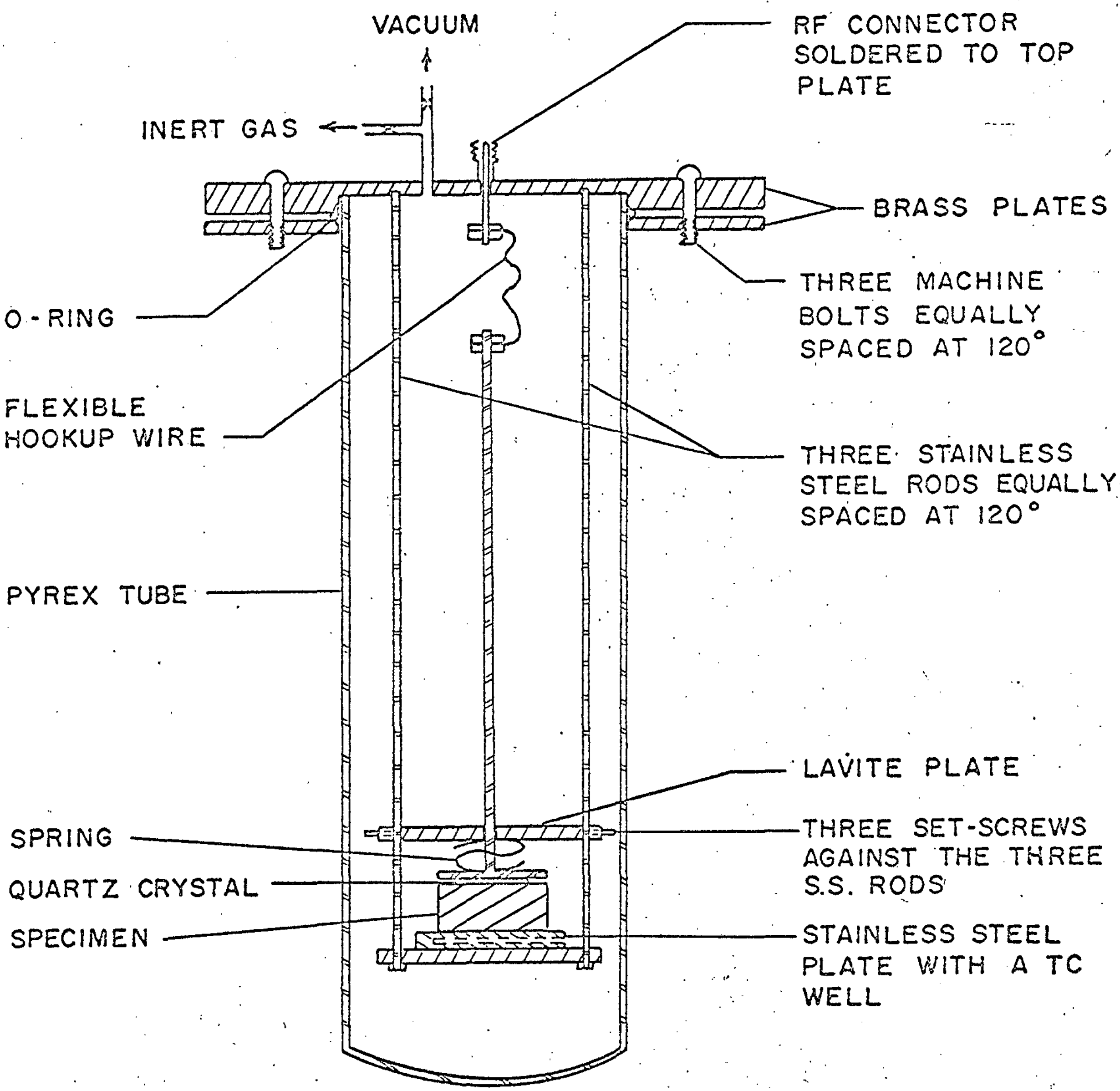

FIG. I EXPERIMENTAL APPARATUS.

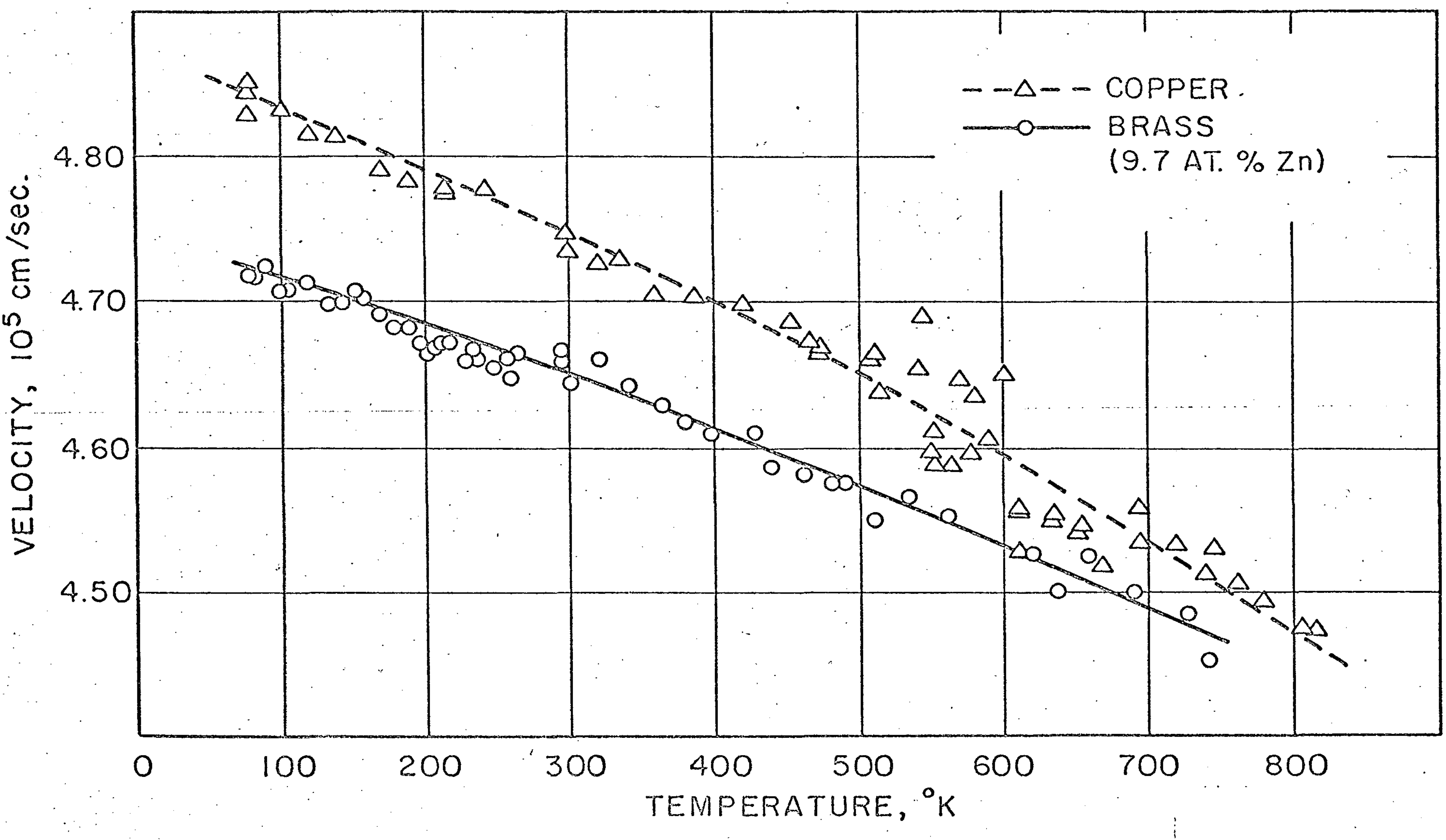

FIG. 2 LONGITUDINAL SONIC VELOCITIES

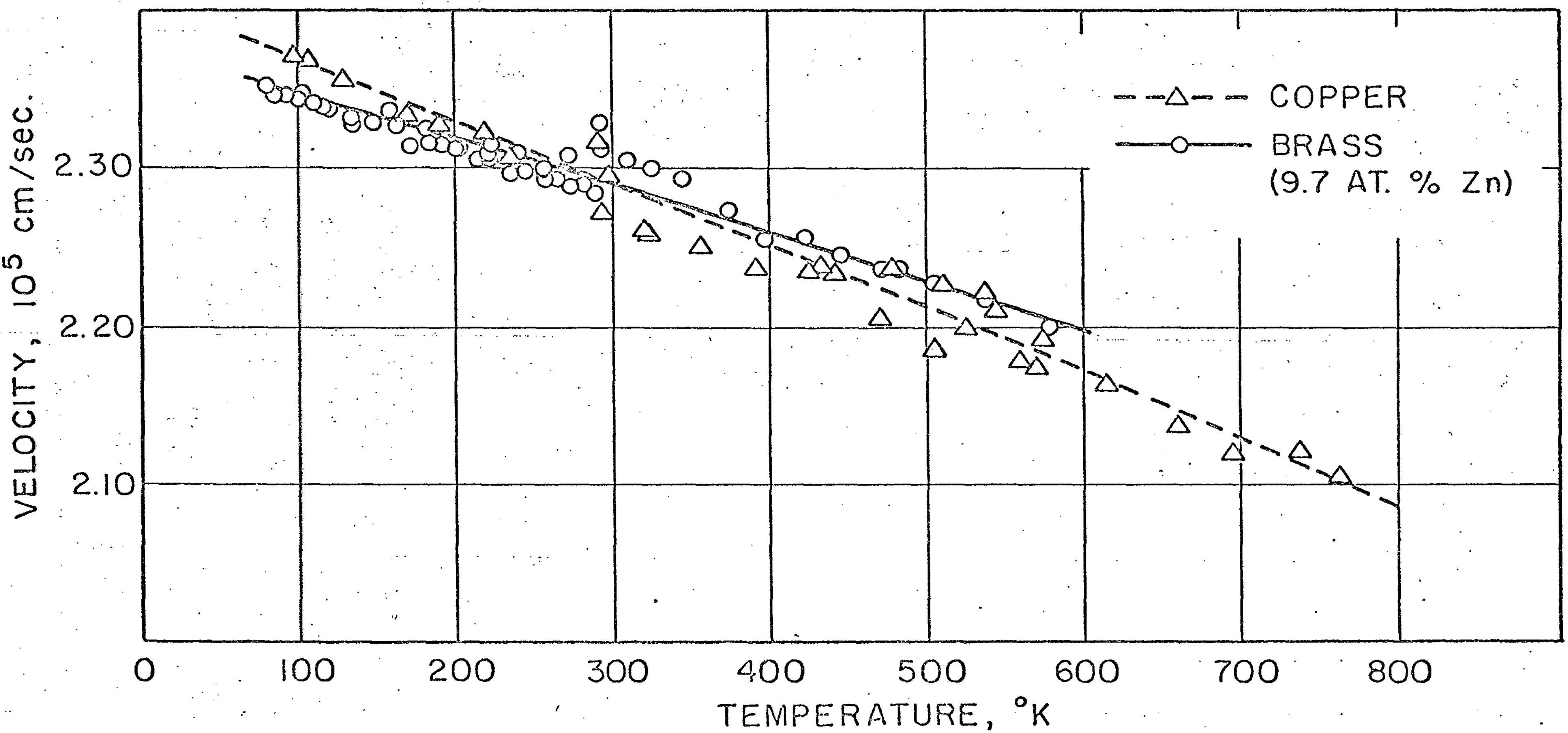

FIG 3 TRANSVERSE SONIC VELOCITIES