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Authors
Chang, Y.A.
Himmel, L.

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University of California

Ernest O. Lawrence Radiation Laboratory

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Y. A. Chang and L. Himmel

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Y. A. Chang* and L. Himmel**

Inorganic Materials Research Division, Lawrence Radiation Laboratory and Department of Mineral Technology, College of Engineering, University of California, Berkeley, California

ABSTRACT

The adiabatic elastic constants of single crystal cadmium have been determined by means of the ultrasonic pulse-echo technique over the temperature interval from 300° to 575°K. The values obtained at 300°K are: $C_{11} = 11.45$, $C_{33} = 5.085$, $C_{66} = 3.750$, $C_{44} = 1.985$ and $C_{13} = 3.99$ in units of 10^{11} dynes/cm^2. The temperature dependences of the linear compressibilities, the Grüneisen parameter and the lattice contribution to the specific heat have been calculated using the elastic constants obtained in the present study and other necessary thermal data available in the literature.

* Present Address: Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California.

** Present Address: University of California, Lawrence Radiation Laboratory, Livermore, California.

INTRODUCTION

Among metals crystallizing in the hexagonal close-packed structure, cadmium and zinc are the only two exhibiting anomalously large values of c/a. Although the occurrence of these large axial ratios is not entirely understood in term of theory, it is clear that the highly anisotropic properties, such as elastic constants, coefficients of thermal expansion and electrical conductivities are associated with these large axial ratios. The elastic constants of cadmium over the temperature interval from 4.2° to 300°K have been determined by Garland and Silverman[1,2]. However, the elastic properties of cadmium from 300°K to its melting point are of special interest, since there is a reversal of the temperature coefficient of the axial ratio within this temperature range[3,4]. Moreover, the elastic properties of zinc from 4.2°K to its melting point obtained by Alers and Neighbours[5] show interesting behavior with respect to compression in the directions parallel and perpendicular to the c-axis. In view of the structural similarities between cadmium and zinc and the reversal of the ~~temperature of the~~ temperature coefficient of the axial ratio for cadmium, it was felt desirable to extend the measurement of the elastic constants of cadmium to temperature near its melting point.

Besides being valuable in the understanding of metallic binding, elastic constants are necessary in computing the Grüneisen parameter and the dilational contribution to the specific heat. This dilational term, which becomes appreciable at high temperatures, must be substracted along with the electronic term from the experimentally determined specific heat at constant pressure in order to obtain the contribution due solely to lattice vibrations.

In the present study, the five elastic constants of cadmium have been

determined from 300° to 575°K using the ultrasonic pulse-echo technique. The compressibilities derived from the elastic constants were used to calculate the Grüneisen parameter and the dilational specific heat. The values of the lattice specific heat at constant volume obtained by substracting the dilational and electronic terms from the experimentally determined values of Cp were then compared with the classical value of 3R at high temperatures.

EXPERIMENTAL PROCEDURE

For a hexagonal crystal, four of the five independent elastic constants, namely C_{11}, C_{33}, C_{44} and C_{66}, may be obtained by measuring the velocities of plane longitudinal waves and appropriately polarized transverse wave propagating in the directions parallel and perpendicular to the c-axis. These velocities are related to the elastic constants according to the following relationship[6,7]:

$$c_{ij} = \rho v^2 \qquad (1)$$

where ρ is the crystal density and v is the appropriate wave velocity in question. The fifth elastic constant, C_{13} must be obtained by measuring the velocities propagating in the direction at an angle ϕ to the c-axis. The velocities of acoustic waves propagating in this direction are related to the elastic constants by the following equations[6,7]:

$$\rho v_t^2 = c_{66}\sin^2\phi + c_{44}\cos^2\phi \qquad (2)$$

$$2\rho v^2 = c_{11}\sin^2\phi + c_{33}\cos^2\phi + c_{44} \pm \left\{ [(c_{11} - c_{44})\sin^2\phi \right.$$
$$\left. - (c_{33} - c_{44})\cos^2\phi]^2 + 4\sin^2\phi \cos^2\phi(c_{13} + c_{44})\right\}^{\frac{1}{2}}$$

The term v_t in equation (2) is the velocity of pure transverse waves propagating in this direction with plane waves polarized perpendicular to the c-axis. The other two velocities as expressed by equation (3) are of mixed character. The plus sign refers to a quasi-longitudinal wave velocity, v_{ql} and the

minus sign refers to a quasi-transverse velocity, v_{qt}. Among the three wave velocities propagating in this direction, the measurement of either v_{ql} or v_{qt} will yield the fifth elastic constant, C_{13}. The other two velocities served to have a check of internal consistency of the data. It is evident from equation (3) that there are two possible mathematical roots for C_{13}. The correct one is determined by the lattice stability condition[8].

In the present study, the growing of three single crystals of 99.999% pure cadmium in the form of 2.5 cm diameter spheres was carried out in an inert atmosphere of high-purity helium in previously outgassed reactor-grade graphite crucibles using a modified Bridgman technique. One specimen with faces normal to the c-axis, a second with faces parallel to the c-axis and a third with faces at an angle of 60° to the c-axis were then cut from each of the three spherical single crystals by electric discharge machining. The orientations of these crystals were determined by back reflection Laue method to within 0.25°. To remove the cold-worked surface layer of these specimens due to electric discharge machining, the crystals were first etched in a solution of nitric acid and methyl alchol (50% acid by volume). After etching, each crystal was then mounted inside a surface ground hardened steel ring of appropriate thickness and polished with 3 micron diamond paste on a vibratory lap (Syntron) until the two faces were flat and parallel to within ±0.0002 cm.

The velocities of acoustic waves were measured by means of a Sperry Products ultrasonic attenuation comparator[9] in a manner described previously[10,11]. X-cut and Y-cut quartz crystals, 1/2-in diameter and resonant at 10 Mc/sec, were used to generate either the pure longitudinal or transverse waves. A special high-temperature epoxy resin consisting of Epon 1031 (Shell Development Co.) and nadic methyl anhydride served as the

bonding agent between the quartz transducer and the cadmium crystals from ambient temperature to about 575°K.

The density of cadmium at 300°K, 8.652 g/cc, used in computing the elastic constants was calculated from x-ray lattice parameters[3]. To correct for the density and the measured sound velocities as a function of temperature, the thermal expansion data of Owen and Roberts[3] were used.

RESULTS

The smoothed values of C_{11}, C_{33}, C_{44} and $\rho v_{q1}^2 (\phi = 22°)$ taken from Fig. 1 are listed in Table I. Also included in this table are the smoothed values of C_{12}, C_{13} and the adiabatic compressibilities parallel and perpendicular to the c-axis: $\chi_{||}$ and $\chi_{\perp}$. The elastic constant C_{12} is not an independent modulus, but related to C_{66} by the equation, $C_{66} = (C_{11} - C_{12})/2$. The values of C_{13} were calculated from the directly measured quantities ρv_{q1}^2 by means of equation (5). The adiabatic compressibilities parallel and perpendicular to the c-axis were derived from the smoothed values of the elastic constants. The appropriate equations are:

$$\chi_{||} = (C_{11} + C_{12} - 2C_{13})/C \qquad (4)$$
$$\chi_{\perp} = (C_{33} - C_{13})/C \qquad (5)$$

where $C = C_{33}(C_{11} + C_{12}) - 2C_{13}^2$. The values of $\chi_{||}$ and $\chi_{\perp}$ are plotted as a function of temperature in Fig. 2.

The number of significant figure displayed 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 temperature. From the statiscal spread or scatter in the experimental data as shown in Fig. 1, the uncertainties in the directly measured quantities: C_{11}, C_{33}, C_{44}, C_{66} and $\rho v_{q1}^2 (\phi = 22°)$ are found to be $\pm 0.5\%$. Using the standard propagation-of-error treatment[12], the uncertainties in the calculated quantities are

as follows: c_{12}, $\pm 1.73\%$; c_{13}, $\pm 3.26\%$; $\chi_{||}$, $\pm 1.17\%$; and $\chi_{\perp}$, $\pm 7.5\%$. Two checks of internal consistency of the data were made at $300°K$. The measured values of $\rho v_{\perp}^2 (\phi = 22°)$ was found to be 0.4% higher than the computed value using equation (2). The second check of internal consistency of the data was made by computing the measured values of $\rho v_{q1}^2 + \rho v_{qt}^2$ at $300°K$ with the calculated value according to the relationship $\rho v_{q1}^2 + \rho v_{qt}^2 = c_{11}\sin^2\phi + c_{33}\cos^2\phi + c_{44}$ (equation 3). Again the difference between the measured and calculated values is about 0.4%.

As shown in Fig. 1, the elastic constants obtained in the present study join smoothly with the low-temperature data of Garland and Silverman[1,2]. The values of c_{11}, c_{33}, c_{44} and c_{66} reported by Abowitz[13] at $300°K$ are in good agreement with our results. Since Garland and Silverman as well as Abowitz used a wrong value of ρ for cadmium at room temperature, all of their reported values of the elastic constants were corrected using the new value calculated from x-ray lattice parameters. The older values of the elastic constants obtained by Grüneisen and Goens[14] as well as Bridgman[15] are also included in Fig. 1 for comparison.

A comparison is also made for the isothermal volume compressibility, χ_V^T derived from the elastic constants, and the directly measured values. The value of χ_V^T obtained in the present study at $300°K$ is $2.21 \times 10^{-11} cm^2/dyne$, using the well-known thermodynamic relationship:

$$\chi_V^T = \chi_V + \alpha^2 TV/C_p \tag{6}$$

where χ_V^T is the isothermal volume compressibility, χ_V is the adiabatic volume compressibility, α ~~is the adiabatic volume compressibility~~ is the volume coefficient of thermal expansion, T is the absolute temperature, and V is the specific volume. The values of α and C_p are available in the literature[3,16]. Bridgman[17], Richards[18] and Adams et. al.[19] have

reported the following values of χ_V^T: 2.10×10^{-11}, 2.10×10^{-11} and

2.25×10^{-11} cm^2/dyne, which are in reasonable agreement with the value obtained

in the present study.

DISCUSSION

For the purpose of comparison, the ratios: C_{66}/C_{44}, C_{11}/C_{33} and $\chi_{||}/\chi_{\perp}$

at $300°$K for eleven metals with hexagonal close-packed structure are listed

in Table II together with the values of c/a taken from the compilation of

Pearson[27]. With the exception of thallium, the elastic anisotropy of

these metals correlates qualitatively with the axial ratios. For cadmium and

zinc, the values of C_{66}/C_{44}, C_{11}/C_{33} and $\chi_{||}/\chi_{\perp}$ are much greater than

unity, presumably due to the anomously large values of c/a.

As shown in Fig. 1, all the elastic constants decrease with increasing

temperature. However, the shear anisotropic factor, $A = C_{66}/C_{44}$, at first

increases with temperature to about $480°$K and then decreases above this

temperature (see Table I). This unusual temperature dependence of A may be

associated with the reversal of the temperature coefficient of the c/a axial

ratio[3,4].

Due to departure from the ideal c/a ratio for cadmium, one expects

the lattice to be more compressible along the c-axis than perpendicular to

the c-axis. This indeed is the case. However, as shown in Fig. 2, $\chi_{||}$ increases

with temperature continuously up to $575°$K, while $\chi_{\perp}$ decreases with temperature.

This is somewhat different from the temperature dependence of the linear

compressibilities for zinc[8]; for which $\chi_{\perp}$ remains constant. Only close

to the melting point does $\chi_{\perp}$ decrease. Since $\chi_{\perp}$ involves the difference

of two large quantities, the discrepancy between the temperature dependences

of $\chi_{\perp}$ for cadmium and zinc may not be real. In any case, the fact that

the temperature dependence for $\chi_{||}$ and $\chi_{\perp}$ are different suggests that

the bonding between the atoms in the basal plane is certainly different from

that between the atoms of adjacent planes. As pointed out previously[2,5], these phenomena are consistent with the model proposed for zinc and cadmium by Wallace[28], who assumes a system of resonating covalent bonds between atoms in the basal plane.

Having the values of $\chi_{||}$ and $\chi_{\perp}$, the values of γ, the Grüneisen parameter, were computed according to the following formula for hexagonal solids:

$$\gamma = (2\beta_{\perp} + \beta_{||})V/(2\chi_{\perp} + \chi_{||})C_p \qquad (7)$$

are plotted in Fig. 5. The terms $\beta_{\perp}$ and $\beta_{||}$ in equation (7) are the coefficients of thermal expansion perpendicular and parallel to the c-axis. The values of γ in Fig. 5 from 300°K down to 10°K are taken from the work of McCammon and White[29]. The Grüneisen parameter γ decreases from 3.4 at 10°K down to 2.17 at about 350°K, and then increases above this temperature. Since there is no theoretical model for predicting the values of γ for anisotropic solids, not much can be said about the temperature dependence of γ for cadmium.

Finally, we have evaluated the lattice contribution to the specific heat from room temperature to 575°K by substracting the dilational and electronic specific heats from the experimentally determined values of C_p. The dilational term was evaluated by means of the thermodynamic relationship:

$$C_p - C_v = \alpha^2 TV/\chi_v^T \qquad (8)$$

where $\alpha = 2\beta_{\perp} + \beta_{||}$ is the volume coefficient of thermal expansion. The electronic contribution, which is a small quantity, was assumed to vary linearly with temperature. The value of the electronic coefficient, $\gamma_{el} = 1.52 \times 10^{-4}$ cal/deg^{2}g-atom was taken from the recent compilation of Hultgren et. al.[16]. The values of the lattice specific heat so obtained at high temperatures approach the classical value of $3R = 5.96$ cal/deg g-atom within the uncertainties of all the experimental quantities involved.

Table I. Elastic Properties of Cadmium. The Adiabatic Elastic Constants and

Values of $\rho v_{q1}^2 (\phi = 22°)$ are in the Units of 10^{11} dyne/cm^2;

The Shear Anisotropic Ratio, $A = c_{66}/c_{44}$ is dimensionless and

Adiabatic Linear Compressibilities are in Units of 10^{-13} cm^2/dyne.

| $T, °K$	c_{11}	c_{33}	c_{66}	c_{44}	ρv_{q1}^2	c_{12}	c_{13}	A	χ_{11}	$\chi_\perp$
300	11.45	5.085	3.750	1.985	6.160	3.95	3.99	1.89	16.0	2.35
320	11.29	5.045	3.680	1.928	6.095	3.93	4.00	1.91	16.1	2.33
340	11.14	5.095	3.605	1.872	6.020	3.93	4.00	1.93	16.3	2.32
360	10.97	4.960	3.520	1.818	5.950	3.93	3.99	1.94	16.4	2.31
380	10.80	4.915	3.435	1.759	5.870	3.93	3.98	1.95	16.6	2.29
400	10.61	4.870	3.340	1.703	5.795	3.93	3.98	1.96	16.8	2.27
420	10.42	4.820	3.240	1.646	5.715	3.94	3.97	1.97	17.0	2.27
440	10.22	4.770	3.135	1.590	5.635	3.95	3.96	1.97	17.2	2.25
460	10.00	4.720	3.025	1.532	5.555	3.95	3.96	1.98	17.5	2.21
480	9.78	4.670	2.910	1.474	5.470	3.96	3.95	1.98	17.7	2.19
500	9.54	4.615	2.785	1.415	5.390	3.97	3.95	1.97	18.0	2.15
520	9.29	4.565	2.655	1.355	5.310	3.98	3.95	1.96	18.3	2.08
540	9.02	4.510	2.520	1.295	5.225	3.98	3.96	1.95	18.6	2.05
560	8.75	4.455	2.385	1.252	5.140	3.96	3.96	1.94	18.9	1.98
575	8.50	4.410	2.280	1.187	5.075	3.94	3.96	1.92	19.2	1.92

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Table II. Comparison of the Axial Ratio, c/a, the Adiabatic Elastic Constant Ratios, C_{66}/C_{44} and C_{11}/C_{33}, and the Adiabatic Linear Compressibility Ratio, $\kappa_{\parallel}/\kappa_{\perp}$ for Cadmium with Those of Other Hexagonal Close-packed Metals

Metals	c/a	C_{66}/C_{44}	C_{11}/C_{33}	$\kappa_{\parallel}/\kappa_{\perp}$	Reference
Cd	1.886	1.89	2.25	6.8	Present Study
Zn	1.855	1.64	2.58	9.0	5
Mg	1.623	1.03	0.96	1.05	20
Co	1.623	0.94	0.86	1.04	21
Re	1.615	1.06	0.90	0.99	22
Tl	1.598	0.372	0.77	0.77	23
Zr	1.593	1.10	0.87	0.86	24
Ti	1.587	0.75	1.11	1.04	24
Hf	1.581	0.93	1.09	0.96	24
Y	1.572	0.97	1.00	1.13	25
Be	1.568	0.82	0.87	0.95	26

Figure Captions:

Fig. 1. The Adiabatic Elastic Constants of Cadmium as a Function of Temperature.

Fig. 2. The Adiabatic Linear Compressibilities of Cadmium as a Function of
Temperature.

Fig. 3. The Grüneisen Parameter of Cadmium as a Function of Temperature.

Fig. 1

Fig. 2

Fig. 3

Fig. 3. XA-chung and F. Hymney
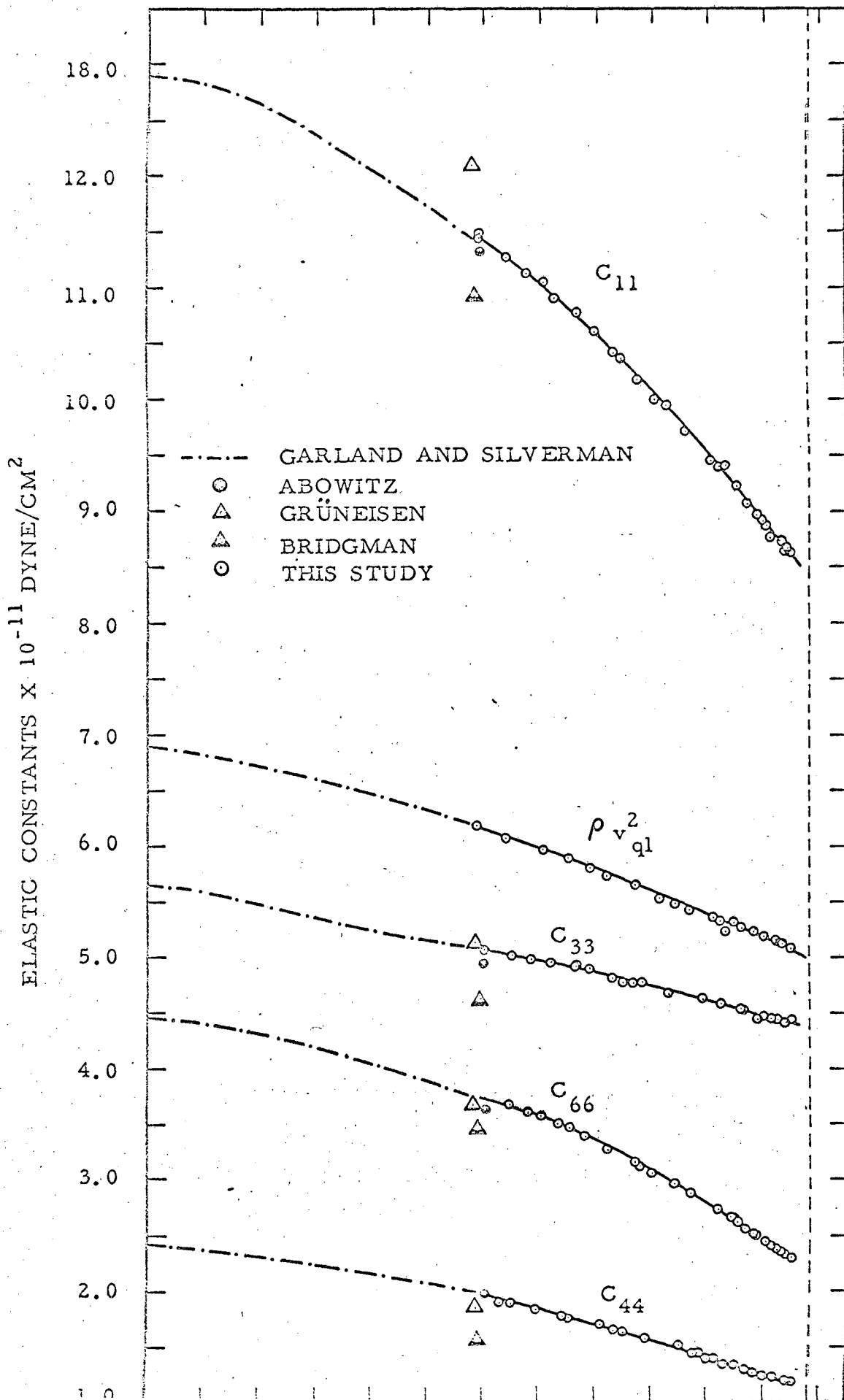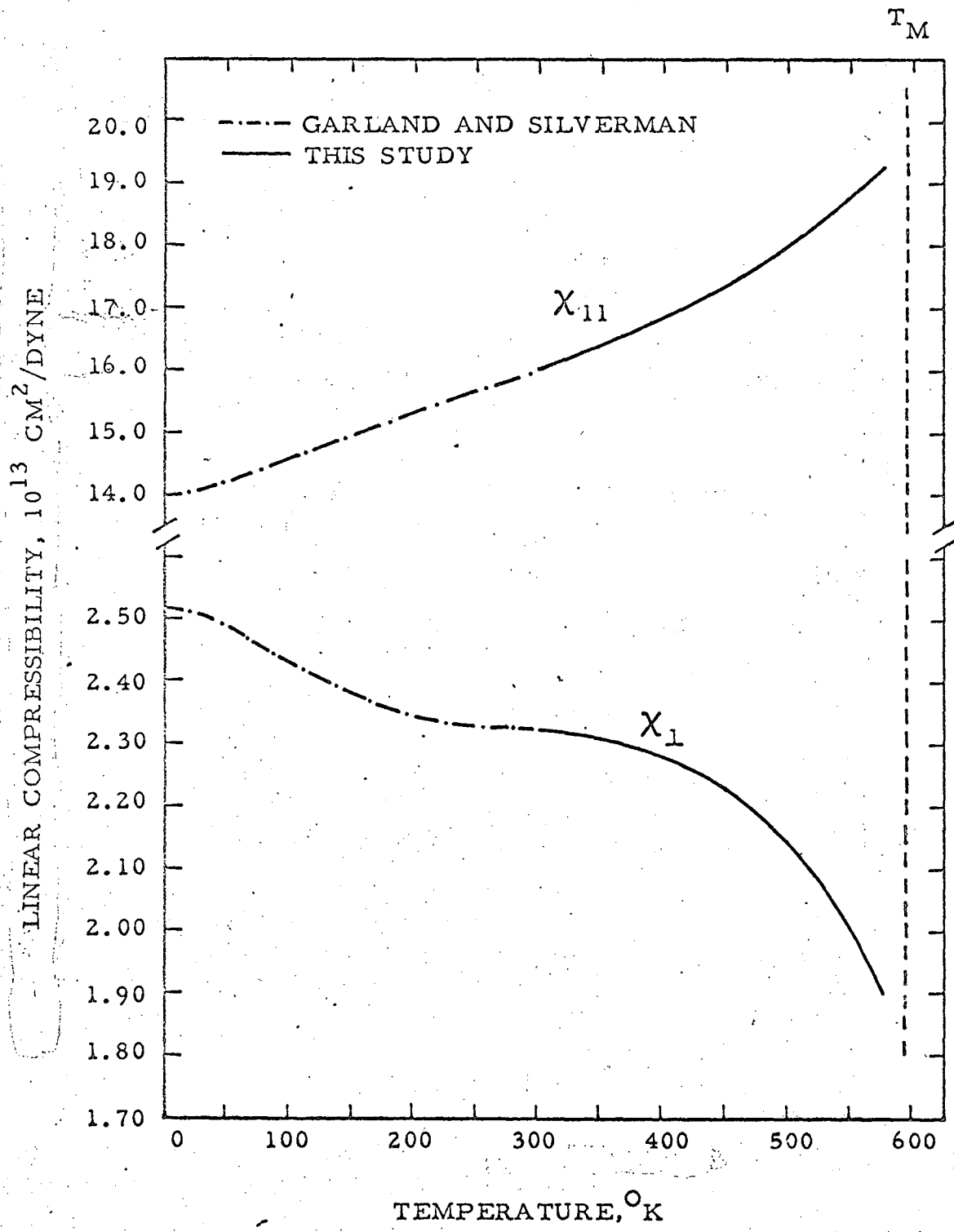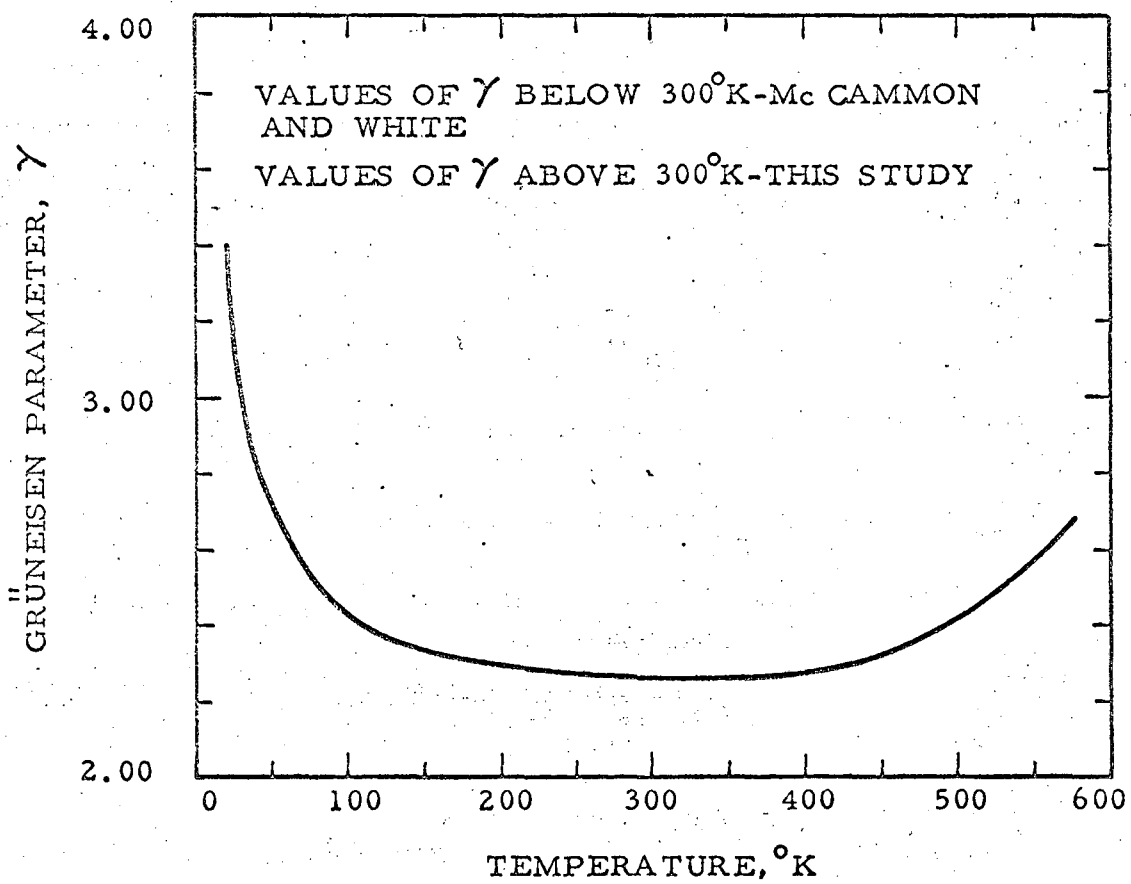
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