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THE ELASTIC PROPERTIES OF COPPER **AND COPPER-NICKEL ALLOYS**

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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January 1971

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Abstract

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The ultrasonic pulse echo technique was used to measure the elastic constants and their pressure derivatives for copper and copper-nickel alloys at temperatures of 297°K, 195°K, and 77°K. Both the elastic constants' explicit temperature dependence at fixed volume and solute concentration and the elastic constants' pure solute concentration dependence at fixed volume and temperature were determined. From these results, it was concluded that the elastic constants of the alloys can be represented by the elastic constants of pure copper plus an additive term which is only a function of solute concentration. The Debye temperature both at fixed pressure and at fixed volume was then calculated; and, its dependence on solute concentration was determined. The Grüneisen parameter calculated from both elastic and thermal data exhibits no significant dependence on solute concentration. The ultrasonic equation of state was then determined and compared with McQueen and Marsh's shock wave data for pure copper. Finally, a comparison of the elastic constants of the copper-nickel alloys was made with the elastic constants of the copper-zinc alloys at both fixed volume and at fixed pressure; and, the results for the shear constants at fixed volume were then compared with Collins' theory.

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INTRODUCTION

In previous publications from this laboratory on the elastic constants of copper alloys^{1,2} and silver alloys,³ the changes in the elastic constants due to alloying have been interpreted in terms of the changes in the long range electrostatic interaction and of the changes in the short range ion-ion repulsive interaction. Other work on lithium alloys by Trivisonno and Smith⁴ and on magnesium alloys by Long and Smith⁵ showed that the shear constants are strongly dependent on contributions from the alloy's non-spherical Fermi surface.

To obtain a better understanding of the ion-ion repulsive interaction, Daniels and Smith⁶ measured the pressure derivatives of the elastic constants of the noble metals. They assumed that the ion-ion repulsive interaction could be represented by a potential which was only a function of the nearest-neighbor separation and then attempted to determine the form of this potential by fitting both the elastic constants and their pressure derivatives to a model consisting of this potential and the contribution from the band structure as calculated by Fuchs.⁷ The first three derivatives of this potential with respect to the nearest neighbor separation are overdetermined by the six pieces of experimental data and could not be fitted to them. To explain the failure of this central force model, it was concluded that the ion-ion repulsive interaction also consisted of a non-central force term. An estimate of the relative magnitude of this non-central force contribution was ob-

tained by calculating a Born-Mayer potential from the bulk modulus and its pressure derivative which was then used to calculate values for the shear constants and their pressure derivatives. The normalized differences between the calculated and experimental values represent the fractional closure failure of this model and were presumed to be an indication of the relative magnitude of this non-central force contribution. The magnitude of these fractional closure failures increases with atomic number as much as an order of magnitude between copper and gold. However, Daniels and Smith did not consider the contributions to the shear constants and their pressure derivatives from the non-spherical Fermi surfaces of the noble metals and their conclusions should be considered with this in mind.

To offer theoretical support for the non-central ion-ion repulsive interaction, Hafemeister⁸ calculated the Born-Mayer potential for the ion-ion repulsive interaction by using an exchange charge model. Although only 25% agreement was obtained with the values obtained by Daniels and Smith, Hafemeister showed that the magnitude of the exchange charge was also a measure of the magnitude of the non-central force contribution to the ion-ion repulsive interaction. The magnitude of these exchange charges followed the same trend with atomic number as Daniels and Smith's fractional closure failures. Since the Fermi surfaces of the noble metals are very similar, any non-central force contribution arising from the conduction electrons should not change appreciably with atomic number. This would indicate that the non-central force term from the ion-

ion repulsive interaction would dominate the non-central force contributions for the heavier noble metals; however, the magnitude of any non-central force contribution from the conduction electrons or from the ion-ion repulsive interaction is still undetermined.

Although the problem of the short range ion-ion interaction is not yet solved, there are various trends in the limiting values of the Debye temperatures which tend to indicate that the changes in the electronic contributions to the elastic constants could be the dominant feature of the noble metal alloys. Rayne⁹ showed that the Debye temperatures of copper-zinc and copper-germanium alloys were not consistent with the Kopp-Neuman relation¹⁰ for the mixing of lattice specific heats given by

$$\frac{1}{\theta^3} = \frac{1-n}{\theta_1^3} + \frac{n}{\theta_2^3} \quad (1)$$

where θ , θ_1 , θ_2 are the Debye temperatures of the alloy, solvent, and solute respectively and n is the solute concentration. The Kopp-Neuman relation predicts an increase in the Debye temperature with solute concentration for copper-germanium alloys and Rayne's measurements showed that it actually decreased with solute concentration. Other investigators¹¹⁻¹⁶ have also shown that most noble metal alloys do not follow this Kopp-Neuman relation or a linear extrapolation to the Debye temperature of the solute. To further investigate these discrepancies, Rayne¹⁷ used the low temperature elastic constants to calculate the Debye temperatures by using the Debye non-dispersive continuum model. Excellent agreement was ob-

tained between the calorimetric values of the Debye temperature measured by Veal and Rayne¹⁸ and the values of the Debye temperature calculated from the elastic constants. Rayne then defined a "reduced" Debye temperature which was effectively only a function of the elastic constants. This "reduced" Debye temperature was strongly dependent on the electron per atom ratio, q . Collins¹⁹ later demonstrated that this is a basic characteristic of most noble metal alloys. The rate of change of molar volume with q is different for different alloys. The elastic constants and this "reduced" Debye temperature change upon alloying from their volume dependence and from the addition of the solute altering both the band structure and the ion-ion repulsive interaction. The precise reason why the "reduced" Debye temperature is dependent on q with the rate of change of molar volume with q being different for different alloys is still not clear.

Although this "reduced" Debye temperature has no real physical significance, Collins¹⁹ attempted to explain the trend of Rayne's "reduced" Debye temperature with q by calculating the contribution to the shear constants at fixed volume produced by the alloys' non-spherical Fermi surfaces. Basing his model on rigid band formalism, he assumed that the short range ion-ion repulsive interaction did not change with alloying and used Fuchs⁷ values, without a screening parameter, for the electrostatic contribution. Although poor agreement for C_{44} was obtained with experiment, he showed that the contributions to the shear constants due to the Fermi surface are fairly large.

The disagreement of Collins' theory with experiment can possibly be traced to the assumption that the ion-ion repulsive interaction is unchanged upon alloying if it were not for the anomalous behavior of the electronic contribution to the specific heat of the noble metal alloys. Measurements of the electronic contribution to the specific heat¹¹⁻¹⁶ have shown that the surface area of the Fermi surface initially increases or only slightly decreases with q whereas the rigid band model predicts a marked decrease. Stern^{20,21} has attempted to explain this anomalous behavior of the electronic specific heat of these alloys. The basic feature of Stern's calculation is that the presence of the solute affects the periodicity of the lattice in such a way as to reduce the influence of the Brillouin zone on the conduction electrons. This results in a change in both the density and corresponding energy of the constant energy surfaces of the conduction electrons. Recent measurements of the electronic specific heat of copper-gold alloys by Martin and Waterhouse²² offer experimental support for Stern's theory. Some of the disagreement of Collins' theory with experiment can be attributed to the failure of the rigid band model to describe the band structure of these alloys; but, the assumption that the ion-ion repulsive interaction remains unchanged upon alloying is still questionable.

The theoretical models presented thus far are inadequate to quantitatively describe the elastic properties of the noble metals and are hard pressed to qualitatively describe the elastic properties of the alloys. Part of this is due to the lack of experimental data on these alloys from which the theorists can base their models. Only

the room temperature elastic constants of the noble metal alloys have been measured with the exception of Rayne's work on the copper-zinc alloys which was done through the temperature range of 300 to 4.2°K. The purpose of this work is to provide a fairly complete description of the copper-nickel alloy system by measuring both the elastic constants and their pressure derivatives at temperatures of 297°K, 195°K and 77°K. For this system q decreases as solute concentration increases and the similarity of this system with the copper-zinc system, where q increases with solute concentration, will permit comparison and correlation of the experimental results with q . Since both the elastic constants and their pressure derivatives are measured, the elastic constants dependence on temperature, volume, and solute concentration can be separated as well as a fairly complete thermodynamic description of the system be presented. By experimentally investigating an alloy system in such depth, it is hoped that some conclusions and insight can be gained about the nature and magnitude of the various contributions to the elastic constants.

EXPERIMENTAL PROCEDURE

The procedure of sample preparation and measurements, of the elastic constants and their pressure derivatives can be found in a previous paper²³ and other articles²⁴⁻²⁷ from this laboratory.

Samples

The four crystals used in this experiment were those grown and used by R.E. Schmunk and C.S. Smith who measured their elastic constants at room temperature.¹ The average composition of these crystals that was previously determined is given in Table 1. The uncertainty in the composition is one half the difference of the chemical analysis of each end of the section used in the ultrasonic measurements. The orientation of all of the crystals was within 2.5 degrees of the [110] axis as determined by back reflection Laue technique.

Elastic Constant Measurements

The buffer technique²⁸ was employed in the measurement of the zero pressure transit times. At 297°K, a polycrystalline aluminum buffer rod was used for the longitudinal wave and a single crystal NaF buffer rod, orientated along [100], was used for the shear waves. The 10 MHz transducer, buffer rod, and crystal were cemented together with Salol and then placed in a bath of Prestone anti-freeze maintained at 297°K. At 195°K, the measurements were made using the polycrystalline aluminum buffer, the cement was Nonaq stop-cock grease and a mixture of Freon - 11 and dry ice was used as a

TABLE 1. The average composition and average gram atomic weight of the copper nickel alloys used in this work.

Crystal	1	2	3	4
Compositon ^a in Atomic % Nickel	0.0	3.02±.02	6.02±.07	9.73±.13
Average Gram Atomic Weight	63.54	63.39	63.25	63.07

a) From R.E. Schmunk and C.S. Smith, Ref. 1.

constant temperature bath. At 77°K, the measurements were made with the polycrystalline aluminum buffer rod using Dow Corning 7 Compound for a cement and liquid nitrogen for a constant temperature bath.

Pressure measurements

The general method of determining the pressure derivatives of the elastic constants from the change in transit time with pressure has been described by Bartels and Schuele.²⁴

Nonaq stopcock grease was used for all bonds at all temperatures. At 297°K, the pressure system consisted of a commercial 60,000 psi hand pump, employing Octoil-S as a pressure transmitting medium, connected to a pressure vessel made of Vascomax 300 maraging steel. The pressure was determined by measuring the change in resistance of a nominal 300 ohm coil of manganin wire maintained at a temperature of $24.0 \pm 0.5^\circ\text{C}$. The coil was calibrated against the freezing point of mercury taken to be 7568 kg/cm^2 at 0°C .²⁹ For each run, the transit time shift was measured at eight pressure values, four while increasing the pressure and four on the down pressure cycle, such that the eight points were approximately 0.44 kbar apart with two points at zero pressure. The maximum pressure was approximately 2.64 kbar. For the various modes, the shifts in the following echoes were measured: C'_{11} - 7th and 8th, C' - 5th and 6th, and C_{44} - 7th and 8th.

At 195°K, the same system was used with the exception of the pressure fluid which was changed to 2-methylpentane, with the

pressure vessel being immersed in a bath of Freeon - 11 and dry ice. At this temperature, the 3rd crystal echo was measured for C' due to a mixing of the C_{44} wave with the C' wave caused by the fact that the 4th and 5th echo transit time of C' were approximately the same as the 7th and 9th echo transit time for C_{44} . There was an obvious beat pattern present in the echo pattern for C' at these echoes indicating a mixing or mode conversion. Pressure runs made with echoes beyond the 3rd gave scattered results differing as much as 3 per cent from the 3rd echo runs. The 3rd echo runs showed the same reproducibility as the other waves and the pressure runs for the other waves showed no sign of this experimental difficulty. Although there was a slight beat present at 297°K for C', the pressure runs were reproduceable from echo to echo. At 77°K, there was no beat present in C' and the echo to echo runs were in excellent agreement.

At 77°K, a pneumatic system consisting of a two stage pneumatic pump capable of a maximum pressure of 30,000 psi with helium gas was used. The pressure was measured with a Heise gage which when checked against the manganin gage showed no detectable difference in the pressure readings. The Berylco 25 berillium copper pressure vessel was immersed in a bath of liquid nitrogen. The same procedure was used as before except that the pressure increments were changed to 5,000 psi and the 8th and 9th echoes were measured for C'_{11} and the 5th and 6th for C'.

The effect of having a transducer of finite thickness cemented on the end of the sample was investigated by cementing a dummy transducer on the other end of the sample and then making a pressure

run at 195°K with the pneumatic system. The dummy transducer was removed and the pressure run repeated. For both shear waves, the two runs agreed well within the limits of experimental uncertainty. For the longitudinal wave, the run with the two transducers appeared slightly larger; but, the experimental uncertainty for this differential experiment is at best 0.75 per cent and the two runs agreed within this limit of experimental uncertainty. The effect of the transducer was therefore neglected.

The difference between the hydraulic and pneumatic system was investigated by making a pressure run at 195°K with the pneumatic system and then placing the same pressure vessel on the hydraulic system without warming it up and repeating the pressure run. The results from using the two pressure media agree within the limits of experimental uncertainty for all waves at this temperature.

Crystal orientation

After all the data was taken, the crystals were etched at the center of their faces, first with pure nitric acid for 60 seconds and then slowly with a solution of 8 grams of ferric chloride, 25 ml, of concentrated HCl, and 100 ml of distilled water for a period of one half hour with constant agitation. Back reflection Laue pictures were then taken using a 3 mil aluminium filter over the film to remove the copper K_{α} fluorescent radiation. From these pictures the direction cosines of the crystals were determined.

RESULTS

The basic data used in the reduction of the experimental results is listed in Table 2. It was necessary to either calculate or modify some of the basic data in order to obtain the data listed in this Table; and, the following is a brief discussion of these calculations and modifications.

The linear coefficient of thermal expansion of copper and copper-nickel alloys has been measured by Aoyama and Itô³¹ in 1939 over the temperature range of 77°K to 273°K. The results of their measurements exhibit some scatter; and, their values for pure copper are in slight disagreement with the later work of Rubin, Altman, and Johnston.³² This later work is judged more reliable due to improvements in the experimental techniques and these values for pure copper will be used in this paper. To obtain the values of the thermal expansion for the alloys that were used in this work, the differences in the thermal expansion between pure copper and these alloys were obtained from Aoyama and Itô's data with a least square interpolation. These differences were then used in conjunction with Rubin, Altman, and Johnston's results to determine the linear coefficient of thermal expansion for the alloys. The smoothed thermal expansion data is plotted as a function of temperature in Figure 1 and the values used in the reduction of the data are listed in Table 2.

The values of the lattice constants and densities at 195°K and 77°K were calculated from the corresponding 297°K values and

TABLE 2. Basic data used in this work for copper and copper-nickel alloys. An Avagadro's number of 6.02305×10^{23} mole⁻¹ was used in the calculation of the X-ray density.

		Composition in At. % Ni.			
		0.0	3.02	6.02	9.73
Lattice (a) Constant (A)	297°K	3.6150	3.6115	3.6081	3.6037
	195°K	3.6090	3.6056	3.6023	3.5981
	77°K	3.6036	3.6003	3.5971	3.5930
	0°K	3.6028	3.5995	3.5963	3.5922
X-ray Density (gm-cm ⁻³)	297°K	8.932	8.937	8.943	8.950
	195°K	8.977	8.981	8.986	8.992
	77°K	9.017	9.021	9.025	9.030
	0°K	9.023	9.027	9.031	9.035
Linear Coef- (b) ficient of Thermal Expansion (10 ⁻⁶ deg ⁻¹)	297°K	16.68	16.53	16.38	16.18
	195°K	15.11	14.92	14.73	14.50
	77°K	7.98	7.88	7.78	7.65
	0°K	0.0	0.0	0.0	0.0
Specific (c) Heat, C _p , (joule mole ⁻¹ deg ⁻¹)	297°K	24.43	24.40	24.36	24.33
	195°K	22.46	22.39	22.35	22.27
	77°K	12.34	12.18	12.03	11.84
	0°K	0.0	0.0	0.0	0.0
Isothermal Bulk Modulus (10 ¹² dyn/cm ⁻²)	297°K	1.3437	1.3499	1.3640	1.3820
	195°K	1.3807	1.3883	1.4030	1.4211
	77°K	1.4212	1.4289	1.4433	1.4575
	0°K	1.429	1.437	1.452	1.466
Crystal Length (cm)	297°K	1.301	1.356	1.413	0.964
	195°K	1.299	1.354	1.411	0.963
	77°K	1.297	1.352	1.409	0.961

- a) The 297°K values for the lattice constant were extrapolated from the results of Ref. 30.
- b) The thermal expansion values were modified by using Ref. 31, 32, and 33 as described in the text.
- c) The values of C_p for pure copper were taken from Ref. 34.

FIGURE 1. The linear coefficient of thermal expansion, α , as a function of temperature for copper and the copper-nickel alloys.

integrated thermal expansion data. Since the thermal expansion for the alloys is not known between 77°K and 0°K, the values of the lattice constants and densities at 0°K were estimated by assuming that the thermal expansion for the alloys was the same as that of pure copper over this temperature interval. The values of the thermal expansion in this temperature range were obtained from the measurements of Carr, McCammon, and White.³³ Since there is only a very slight change in the lattice parameter and density between 77°K and 0°K, the error induced by this assumption is quite small and may be neglected.

The molar specific heat at constant pressure, C_p , is needed to calculate the isothermal bulk modulus, B_T , however, no experimental data exists for the molar specific heat of the alloys at constant pressure. Therefore, the following scheme was used to estimate this quantity. The measured elastic constants were used to calculate the ultrasonic Debye temperature for pure copper and the copper-nickel alloys. Since this is not the same as the thermodynamic Debye temperature, it was assumed that the per cent difference between the ultrasonic Debye temperature of the alloys and that of pure copper was the same as the per cent difference between the thermodynamic Debye temperature of the alloys and that of pure copper. With the use of tables, the thermodynamic Debye temperature for pure copper was calculated from the molar specific heat at constant volume, C_V , calculated from the thermodynamic relation

$$\frac{C_p}{C_V} = 1 + \frac{T V \beta^2 B_s}{C_p} \quad (2)$$

where V is the molar volume, β the volume coefficient of thermal expansion, T the absolute temperature, and B_s the adiabatic bulk modulus. The thermodynamic Debye temperatures were then calculated for the alloys and the specific heat at constant volume was then obtained with the use of tables. Finally, the specific heat at constant pressure was calculated using Eq. 2. The isothermal bulk modulus was then calculated from the measured adiabatic bulk modulus using the thermodynamic relation

$$\frac{B_s}{B_T} = 1 + \frac{T V \beta^2 B_s}{C_p} \quad (3)$$

Elastic constants

Since copper and copper-nickel alloys are cubic crystals, the three independent elastic constants can be determined from the velocities of the three sound waves propagated along the $[110]$ direction. Measurement of the longitudinal velocity, v_1 , gives

$$\rho v_1^2 = C'_{11} = \frac{C_{11} + C_{12} + 2C_{44}}{2} \quad (4)$$

while measurements of the two shear velocities, v_2 and v_3 , give

$$\rho v_2^2 = C_{44} \quad (5)$$

and

$$\rho v_3^2 = C' = \frac{C_{11} - C_{12}}{2} \quad (6)$$

Here ρ is the density and the velocity is computed from

$v_i = 2L/t_i$ where L is the sample length and t_i is the transit

time. The adiabatic bulk modulus is computed from

$$B_s = C'_{11} - C_{44} - C'/3 \quad (7)$$

From three to five acoustic echoes were observed for each sample-buffer rod combination. The 1st - 2nd echo transit time showed a systematic variation from the succeeding echo-to-echo transit times. Wong and Schuele³⁴ give a qualitative explanation for this. Although more echoes would be measured, only the 2nd - 3rd echo transit times were used. The perturbation calculation of Neighbors³⁵ was used to correct for the slight misorientation of the crystals determined from back reflection Laue photographs. Only C' was fairly sensitive to this correction changing 0.8% for the pure copper crystal which was 2.5 degrees off the [110] axis. The experimental uncertainties of the various elastic constants are: $C'_{11} - 0.2\%$, $C' - 0.3\%$, $C_{44} - 0.2\%$, $C_{12} - 0.4\%$, $C_{11} - 0.3\%$, $B_s - 0.35\%$. The elastic constants of copper and copper-nickel alloys when plotted against molar volume are found to be linear and the 0°K elastic constants were then determined by extrapolating these plots to the molar volume at 0°K.

The results of the elastic constant measurements for pure copper are given in Table 3 along with the results of other investigators, with agreement being quite satisfactory. The experimental results of the room temperature elastic constant measurements for pure copper and copper-nickel alloys at room temperature are given in Table 4 along with those of Schmunk and Smith.¹ The experimental results are in agreement with Schmunk and Smith's within the limits

TABLE 3. The adiabatic elastic constants for copper in units of 10^{12} dyn/cm². Not all figures are significant.

Description	C_{44}	C'	C'_{11}	C_{11}	C_{12}	B_s
Chang and (a) Himmel 300°K	0.758	0.2355	2.220	1.700	1.225	1.385
Schmunk and (b) Smith 300°K	0.7511	0.2332	2.199	1.681	1.215	1.370
Goens room (c) temperature	0.753	0.236	2.215	1.698	1.226	1.383
Overton and (d) Gaffney 300°K	0.7539	0.2348	2.2030	1.6839	1.2142	1.3708
Hike and (e) Granato room temperature	0.756	0.236	2.230	1.710	1.239	1.396
Author 297°K	0.7556	0.2342	2.2174	1.6960	1.2270	1.3838
Overton and (d) Gaffney 190°K	0.7841	0.2458	2.2608	1.7225	1.2309	1.3948
Author 195°K	0.7816	0.2447	2.2685	1.7316	1.2422	1.4053
Overton and (d) Gaffney 80°K	0.8100	0.2546	2.3094	1.7540	1.2447	1.4145
Goens and (f) Weerts 80°K	0.803	0.252	2.314	1.763	1.259	1.427
Author 77°K	0.8086	0.2561	2.3207	1.7682	1.2560	1.4268
Overton and (d) Gaffney 0°K	0.8177	0.2564	2.3234	1.7620	1.2494	1.4203
Rayne 4.2°K (g)	0.814	0.260	2.316	1.760	1.238	1.415
Author 0°K (Extrapolated)	0.812	0.257	2.327	1.772	1.258	1.429

TABLE 3. - continued

- (a) See Ref. 36
- (b) See Ref. 1
- (c) See Ref. 37
- (d) See Ref. 38
- (e) See Ref. 39
- (f) See Ref. 40
- (g) See Ref. 17

TABLE 4. Comparison of the room temperature elastic constants of copper and copper-nickel alloys in units of 10^{12} dyn/cm². Not all figures are significant.

Investigator	At. % Ni.	C_{44}	C'	B_s
Schmunk and Smith ^(a)	0.0	0.7511	0.2332	1.370
Author	0.0	0.7556	0.2342	1.3838
Schmunk and Smith ^(a)	3.02	0.7674	0.2375	1.377
Author	3.02	0.7684	0.2402	1.3896
Schmunk and Smith ^(a)	6.02	0.7812	0.2434	1.386
Author	6.02	0.7828	0.2444	1.4037
Schmunk and Smith ^(a)	9.73	0.7909	0.2489	1.392
Author	9.73	0.7960	0.2490	1.4217

(a) See Ref. 1.

of experimental uncertainty with the exception of B_s for the 9.73% Ni alloy. The reason Schmunk and Smith's values are consistently lower is due to the differences in the ultrasonic pulse echo techniques used and the fact that the buffer rod technique was employed in this work to minimize any transit time error due to the finite thickness of the transducer.

The results for the adiabatic elastic constants and the isothermal bulk modulus for pure copper and the copper-nickel alloys are listed in Table 5 and their dependence on temperature is shown in Figures 2 through 6. All of the elastic constants increase with nickel concentration, as much as 6 per cent for C' and as little as 2.5 per cent for B_s . Within the limits of experimental error, all the alloys have the same temperature dependence as the solvent. This means that the net change in the zero pressure elastic constants due to alloying is independent of temperature and dependent only on nickel concentration.

Pressure results

For a pressure run, the shift of the n th echo transit time was plotted against the change in resistance of the manganin pressure gage or the change in pressure for the Heise gage. Linear plots were obtained for all runs and a least square fit was used to obtain the slope. The number of runs taken for each wave at each temperature varied from three to six. The pressure derivatives of the elastic constants were calculated by averaging the slopes and using the relation

TABLE 5. The adiabatic elastic constant and isothermal bulk modulus for copper and copper nickel alloys in 10^{12} dyn/cm². Not all figures are significant and the 0°K values are extrapolated from the higher temperature values.

Elastic Constant	Temperature	Composition in At. % Nickel			
		0.0	3.02	6.02	9.73
C'_{11}	297°K	2.2174	2.2381	2.2680	2.3008
	195°K	2.2685	2.2913	2.3210	2.3536
	77°K	2.3207	2.3443	2.3738	2.4033
	0°K	2.327	2.351	2.380	2.411
C'	297°K	0.2342	0.2402	0.2444	0.2490
	195°K	0.2447	0.2509	0.2552	0.2579
	77°K	0.2561	0.2618	0.2664	0.2709
	0°K	0.257	0.263	0.268	0.272
C_{44}	297°K	0.7556	0.7684	0.7828	0.7960
	195°K	0.7816	0.7953	0.8089	0.8222
	77°K	0.8086	0.8227	0.8362	0.8501
	0°K	0.812	0.826	0.839	0.853
B_s	297°K	1.3838	1.3896	1.4037	1.4217
	195°K	1.4053	1.4123	1.4270	1.4448
	77°K	1.4268	1.4343	1.4487	1.4629
	0°K	1.429	1.437	1.452	1.466
B_T	297°K	1.3437	1.3499	1.3640	1.3820
	195°K	1.3807	1.3883	1.4030	1.4211
	77°K	1.4212	1.4289	1.4433	1.4575
	0°K	1.429	1.437	1.452	1.466

FIGURE 2. The elastic constant C' as a function of temperature for copper and the copper-nickel alloys.

FIGURE 3. The elastic constant C_{44} as a function of temperature for copper and the copper-nickel alloys.

FIGURE 4. The elastic constant C'_{11} as a function of temperature for copper and the copper-nickel alloys.

FIGURE 5. The adiabatic bulk modulus, B_S , as a function of temperature for copper and the copper-nickel alloys.

FIGURE 6. The isothermal bulk modulus, B_T , as a function of temperature for copper and the copper-nickel alloys.

$$\left(\frac{\partial C}{\partial p}\right)_T = C \left[\frac{1}{3B_T} - 2 \left(\frac{\partial \ln t}{\partial p} \right)_T \right] \quad (8)$$

where t is the transit time and p is the pressure. The pressure derivatives were corrected for misorientation of the crystals by using the perturbation correction described by Fontanella and Schuele.⁴¹ The correction to the pressure derivatives was small with the exception of $(\partial C'/\partial p)_T$ which was very sensitive to these corrections changing slightly more than 1 per cent for the pure copper crystal which was off orientation 2.5 degrees. The 0°K pressure derivatives were determined by extrapolating the pressure derivatives as a function of molar volume to the molar volume at 0°K in the spirit of the quasi-harmonic approximation. The pressure derivative of the isothermal bulk modulus was calculated by using the equation developed by Overton.⁴²

At 77°K, the main uncertainty is due to the standard deviation of the average of the slopes of 0.5 per cent or less. The other uncertainties are due to the pressure gage calibration, the time delay calibration of the oscilloscope, and the uncertainty in the elastic constants. The experimental uncertainty of the directly measured pressure derivatives was set at 1 per cent and the uncertainty of $(\partial B_S/\partial p)_T$ was set at 2 per cent. At the higher temperatures the bonds between the crystal and the transducer were poorer as demonstrated from ringing in the echo pattern. At this temperature there was more scatter in the data and consequently a larger experimental uncertainty. The experimental uncertainty in the directly measured pressure derivatives at 195°K was set at 1.5 per cent and

at 297°K at 2 per cent. For $(\partial B_s / \partial p)_T$, the experimental uncertainty was set at 2.5 per cent and 2 per cent for 195 and 297°K.

The results of the adiabatic pressure derivatives for pure copper are given in Table 6 along with those of other investigators. Salama and Alers⁴³ used third order elastic constants to calculate the hydrostatic pressure derivatives which could explain some of the obvious discrepancies. Lazarus⁴⁴ was the first to measure the pressure derivatives with a pulse technique in 1949 and his values for $(\partial C'_{11} / \partial p)_T$ and $(\partial C_{44} / \partial p)_T$ appear quite low. Daniels and Smith⁶ used a pulse echo technique and their data was reduced using Bridgemen's value for the freezing point of mercury⁴⁷ as a pressure calibration. By using the present value for the freezing point of mercury,²⁹ their values would be lowered by 1 per cent which would place them in excellent agreement with the author's with the exception of $(\partial C' / \partial p)_T$ which is 3 per cent larger. Hiki and Granato³⁹ used a sensitive ultrasonic interference method and only a maximum pressure of 60 bars and their results for the shear waves are in poor agreement with the other investigator's. The other investigators used a maximum pressure from 2.5 to 10 kbar and none of them reported observing any nonlinear pressure dependence of the measured transit times and/or repetition frequency. The reason for Hiki and Granato's poor agreement may be due to dislocation motion at low pressure which is pinned at high pressure. Ho, Pourier, and Ruoff⁴⁶ used a phase comparison method obtaining results good to 5 per cent which places them in agreement with the author's within the limits of experimental uncertainty with the exception of $(\partial C' / \partial p)_T$ which is 10 per cent

TABLE 6. The isothermal pressure derivatives of the adiabatic elastic constants for copper.

Description	$\left(\frac{\partial C'_{11}}{\partial p}\right)_T$	$\left(\frac{\partial C'}{\partial p}\right)_T$	$\left(\frac{\partial C_{44}}{\partial p}\right)_T$	$\left(\frac{\partial C_{11}}{\partial p}\right)_T$	$\left(\frac{\partial C_{12}}{\partial p}\right)_T$	$\left(\frac{\partial B_s}{\partial p}\right)_T$
Salama and Alers ^(a) 295°K	8.45	0.45	2.5	6.4	5.5	5.8
Lazarus ^(b) room temperature	4.93	0.566	0.83	4.67	3.53	3.91
Daniels and Smith ^(c) room temperature	8.13	0.580	2.35	6.36	5.20	5.59
Hiki and Granato ^(d) room temperature	8.195	0.375	2.63	5.94	5.19	5.44
Ho, Poirier, ^(e) and Ruoff 295°K	7.68	0.50	2.24	5.95	4.94	5.28
Author 297°K	7.97	0.556	2.33	6.19	5.08	5.45

TABLE 6. -- Continued

Description	$\left(\frac{\partial C'_{11}}{\partial p}\right)_T$	$\left(\frac{\partial C'}{\partial p}\right)_T$	$\left(\frac{\partial C_{44}}{\partial p}\right)_T$	$\left(\frac{\partial C_{11}}{\partial p}\right)_T$	$\left(\frac{\partial C_{12}}{\partial p}\right)_T$	$\left(\frac{\partial B_s}{\partial p}\right)_T$
Ho, Poirier, and Ruoff 77°K	7.92	0.50	2.46	5.95	4.96	5.29
Author 77°K	7.74	0.567	2.32	5.99	4.85	5.23

(a) See Ref. 43

(b) See Ref. 44

(c) See Ref. 6

(d) See Ref. 45

(e) See Ref. 46

lower; however, they did not measure $(\partial C'/\partial p)_T$ directly.

The experimental results of the pressure derivatives of the elastic constants for copper and the copper-nickel alloys are given in Table 7. At 297°K there appears to be no measurable change in the pressure derivatives of the elastic constants with solute concentration with the exception of an initial jump of 4 per cent in $(\partial C'/\partial p)_T$ between pure copper and the 3.02% Ni alloy. This initial jump is still present at 195°K with a net change of 6 per cent in $(\partial C'/\partial p)_T$ between pure copper and the 9.73% Ni alloy, while $(\partial C'_{11}/\partial p)_T$ appears to increase 3 per cent over this range, $(\partial C_{44}/\partial p)_T$ appears to increase 2 per cent, and both $(\partial B_S/\partial p)_T$ and $(\partial B_T/\partial p)_T$ show an approximate increase of 4 per cent. At 77°K there appears to be no change or very little change in the pressure derivatives with solute concentration. The pressure derivatives of the shear waves are fairly temperature independent exhibiting only a 1 to 2 per cent decrease from 297° to 0°K while $(\partial C'_{11}/\partial p)_T$ shows a 3 to 4 per cent decrease over this range, $(\partial B_S/\partial p)_T$ decreases 5 per cent, and $(\partial B_T/\partial p)_T$ shows a decrease of 6 per cent.

TABLE 7. The isothermal pressure derivatives of the adiabatic elastic constants and the isothermal bulk modulus of copper and copper nickel alloys. The 0°K values were extrapolated from the higher temperature values..

Pressure Derivative	Temperature	Composition in At. % Nickel			
		0.0	3.02	6.02	9.73
$\left(\frac{\partial C'_{11}}{\partial p}\right)_T$	297°K	7.97	8.03	8.00	8.02
	195°K	7.62	7.75	7.73	7.87
	77°K	7.74	7.72	7.67	7.76
	0°K	7.73	7.71	7.66	7.73
$\left(\frac{\partial C'}{\partial p}\right)_T$	297°K	0.556	0.578	0.579	0.575
	195°K	0.545	0.565	0.567	0.577
	77°K	0.567	0.565	0.568	0.569
	0°K	0.568	0.565	0.567	0.568
$\left(\frac{\partial C_{44}}{\partial p}\right)_T$	297°K	2.33	2.33	2.36	2.35
	195°K	2.29	2.31	2.34	2.33
	77°K	2.32	2.30	2.30	2.34
	0°K	2.32	2.30	2.30	2.33
$\left(\frac{\partial B_s}{\partial p}\right)_T$	297°K	5.45	5.51	5.45	5.48
	195°K	5.15	5.25	5.21	5.35
	77°K	5.23	5.23	5.18	5.23
	0°K	5.22	5.22	5.17	5.21
$\left(\frac{\partial B_T}{\partial p}\right)_T$	297°K	5.51	5.57	5.50	5.53
	195°K	5.19	5.28	5.24	5.37
	77°K	5.23	5.23	5.18	5.23
	0°K	5.22	5.22	5.17	5.21

INTERPRETATION

It was stated in the Introduction that the present theoretical models do not adequately describe the elastic properties of the noble metal alloys. It will then be beneficial to first ascertain as much experimental information for this alloy system as possible before investigating its microscopic properties. Initially, the various experimental properties will only be discussed in terms of either the crystal's internal energy or the crystal's Helmholtz free energy from which these properties can in principle be calculated. Since the crystal's internal energy and Helmholtz free energy are thermodynamic potentials, all the experimental properties will be presented within the basic framework of thermodynamics. This may make the topics of the next section appear somewhat unrelated; but, it is hoped that in the Microscopic Interpretation section, when the specific details of the composition of the crystal's internal energy are discussed, the experimental calculations of the following section will become somewhat unified.

THERMODYNAMIC CALCULATIONS

The thermodynamics of the copper-nickel alloy system will be analyzed by first investigating the thermodynamics of the elastic constants themselves. Since the pressure derivatives of the elastic constants were also measured, the dependence of the elastic constants on temperature, volume, and solute concentration may be separated. The Debye temperature will then be calculated from the extrapolated 0°K elastic constants by using the Debye non-dispersive continuum model; and, the Debye temperature's dependence on volume, solute concentration, and average mass will be determined. From the elastic constants and their pressure derivatives, the Gruneisen parameter will be calculated; and, for completeness the ultrasonic equation of state for this alloy system will be presented.

The Thermodynamics of the Elastic Constants

The adiabatic elastic constants are defined as the second partial derivative of the crystal's internal energy per unit volume with respect to the appropriate strain at constant entropy; and, the isothermal elastic constants are defined as the second partial derivative of the Helmholtz free energy per unit volume with respect to the appropriate strain at constant temperature. The elastic constants are therefore an intensive thermodynamic property of the system; and, they can then be considered to be functions of any three independent thermodynamic variables of the system. It is theoretically advantageous to choose these three independent thermodynamic variables as: temperature, T ; volume, V ; and solute concen-

tration, η . An elastic constant, C , can now be written as

$$C = C(T, V, \eta). \quad (9)$$

The dependence of an elastic constant on these variables is fairly straight forward. The explicit temperature dependence of an elastic constant at constant V and η is produced by the anharmonic character of the crystal's internal energy. This anharmonicity also produces the dependence of an elastic constant on volume at constant T and η . Finally, the dependence of an elastic constant on solute concentration at constant T and V is determined solely from the addition of the solute altering the crystal's internal energy.

The dependence of an elastic constant on these thermodynamic variables is of direct interest to the theoretician. However, the elastic constants were measured at constant pressure; and, therefore, the experimental thermodynamic variables are T , P , and η instead of the desired T , V , and η . The variation of the elastic constants on these experimental thermodynamic variables is a mixture of the dependencies of the elastic constants on the desired variables. For example, when one varies the temperature at fixed P and η , one finds that the crystal's volume changes from thermal expansion. The variation of a measured elastic constant at fixed P and η with temperature is then due to both the elastic constant's volume dependence and explicit temperature dependence. Similarly, when the solute concentration is changed at fixed T and P , the crystal's volume is also changed. Therefore, the variation of a measured elastic constant at T and P with solute concentration is due to both the elastic con-

stant's volume dependence and pure solute concentration dependence.

In order to determine the effect of T , V , and n on the elastic constants, one must convert from the measured system of variables to the desired system of variables via thermodynamics relations. It is therefore necessary to calculate isochoric elastic constants from the measured isobaric elastic constants in order to separate out the dependence of the elastic constants on temperature, volume, and solute concentration. The experimentally determined pressure derivative of an elastic constant is a measure of the anharmonicity of the crystal's internal energy and are related to the volume dependence of the elastic constant. At fixed T and n , an elastic constant may be expressed in the following Taylor series

$$C(T, V, n) = C(T, V_0, n) + \left(\frac{\partial C}{\partial V} \right)_{T, n} \bigg|_{V_0} (V - V_0) + \frac{1}{2} \left(\frac{\partial^2 C}{\partial V^2} \right)_{T, n} \bigg|_{V_0} (V - V_0)^2 + \dots \quad (10)$$

where V_0 is the volume at which the measurements were made and all derivatives are evaluated at this volume as denoted by the subscript, V_0 . This series does not converge rapidly for volume changes larger than one per cent; consequently, the addition of the second derivative of the elastic constant with respect to volume and possibly higher derivatives may be necessary.

The first derivative of the elastic constant with respect to

volume can be expressed as

$$\left(\frac{\partial C}{\partial V}\right)_{T,\eta} = \left(\frac{\partial P}{\partial V}\right)_{T,\eta} \left(\frac{\partial C}{\partial P}\right)_{T,\eta} \quad (11)$$

Since

$$B_T(T, V, \eta) = -V \left(\frac{\partial P}{\partial V}\right)_{T,\eta} \quad (12)$$

$$\left(\frac{\partial C}{\partial V}\right)_{T,\eta} = -\frac{B_T(T, V, \eta)}{V} \left(\frac{\partial C}{\partial P}\right)_{T,\eta} \quad (13)$$

This expression could be differentiated again to determine the second derivative of the elastic constants with respect to volume if the second derivative of the elastic constants with respect to pressure were known. The experimental measurements show that the measured shift in the transit time is linear in pressure; and, from this result we will assume that the second derivative of the elastic constant with respect to pressure is small and will be neglected.⁴⁸ Differentiating the above expression with respect to volume under this assumption yields

$$\left(\frac{\partial^2 C}{\partial V^2}\right)_{T,\eta} = +\frac{B_T(T, V, \eta)}{V^2} \left[\left(\frac{\partial B_T}{\partial P}\right)_{T,\eta} + 1 \right] \left(\frac{\partial C}{\partial P}\right)_{T,\eta} \quad (14)$$

The Taylor series may now be expressed in terms of the pressure derivatives as

$$\begin{aligned}
 C(T, V, \eta) = & C(T, V_0, \eta) - B_T(T, V_0, \eta) \left(\frac{\partial C}{\partial P} \right)_{T, \eta} \left(\frac{V - V_0}{V_0} \right) \\
 & + \frac{1}{2} B_T(T, V_0, \eta) \left[\left(\frac{\partial B_T}{\partial P} \right)_{T, \eta} + 1 \right] \left(\frac{\partial C}{\partial P} \right)_{T, \eta} \left(\frac{V - V_0}{V_0} \right)^2 \\
 & + \dots
 \end{aligned}
 \tag{15}$$

where V_0 is the volume at which the measurements were made. This equation allows one to correct for the volume change from thermal expansion as well as for the volume change upon alloying.

At fixed T and η , the isochoric elastic constants at the volume of the crystal at 0°K can now be calculated. The variation of these isochoric elastic constants with temperature at fixed η is then due solely to their explicit temperature dependence. The difference between these isochoric elastic constants and the measured isobaric elastic constants at fixed T and η is merely the change in the measured elastic constants due to their volume dependence. The isochoric elastic constants at the volume of the solvent at the temperature the measurements were made can also be calculated. The variation of these isochoric elastic constants with solute concentration at fixed T is due only to their pure solute concentration dependence. Again, the difference between the isochoric elastic constants and the measured isobaric elastic constants is due to the elastic constants' volume dependence.

Now that a scheme has been developed for separating the dependence of the measured elastic constants on temperature, volume, and solute concentration a choice will be made as to which three independent elastic constants will be examined. It is theoretically advantageous that the three independent elastic constants C' , C_{44} , and bulk modulus be examined. The reason is that the two shear constants C' and C_{44} correspond, in first order, to a shear deformation at constant volume and the bulk modulus corresponds to a uniform compression with no shear. It can be shown by using thermodynamic arguments that the adiabatic and isothermal shear constants are identical whereas there is a difference between the adiabatic and isothermal bulk modulus except at absolute zero. A complete discussion of these three independent elastic constants will then describe the second order elastic properties of the entire system.

Shear Constants

The isochoric shear constants have been calculated at the volume of the alloy, V'' , at 0°K as a function of temperature, and, the results of this calculation are listed in Table 8. Upon careful inspection of these results, the net change with temperature of these isochoric elastic constants is independent of solute concentration within the limits of experimental uncertainty. This was also shown to be the case for the directly measured isobaric shear constants. For clarity, the dependence of the isochoric and isobaric shear constants C' and C_{44} on temperature for only pure copper and the 9.73 atomic per cent nickel alloy are shown in Figures 7 and 8. From

TABLE 8. The isochoric elastic constants at the volume of the crystal, V'' , at 0°K in units of 10^{12} dyn/cm². The 0°K values were extrapolated from the higher temperature values.

Isochoric Elastic Constant	Temperature	Concentration in At. % Nickel			
		0.0	3.02	6.02	9.73
$C' (V'')$	297°K	0.242	0.248	0.252	0.257
	195°K	0.249	0.255	0.259	0.264
	77°K	0.257	0.262	0.267	0.272
	0°K	0.257	0.263	0.268	0.272
$C_{44} (V'')$	297°K	0.789	0.801	0.816	0.829
	195°K	0.799	0.812	0.826	0.839
	77°K	0.811	0.825	0.839	0.853
	0°K	0.812	0.826	0.839	0.853
$B_S (V'')$	297°K	1.461	1.467	1.480	1.498
	195°K	1.444	1.451	1.466	1.484
	77°K	1.433	1.440	1.455	1.469
	0°K	1.429	1.437	1.452	1.466
$B_T (V'')$	297°K	1.422	1.430	1.441	1.459
	195°K	1.420	1.428	1.442	1.461
	77°K	1.427	1.435	1.449	1.464
	0°K	1.429	1.437	1.452	1.466

FIGURE 7. The isobaric shear constant $C'(P=0)$ and the isochoric shear constant $C'(V'')$ at the volume, V'' , of the crystal at 0°K as a function of temperature for copper and the 9.73 at. % Ni alloy.

FIGURE 8. The isobaric shear constant $C_{44}(P=0)$ and the isochoric shear constant $C_{44}(V'')$ at the volume, V'' , of the crystal at 0°K as a function of temperature for copper and the 9.73 at. % Ni. alloy.

these Figures, it can be seen that both the isochoric and isobaric shear constants decrease with increasing temperature. The elastic constants' explicit temperature dependence represents approximately 2/3 of the decrease of the isobaric C' with temperature and approximately 1/2 of the decrease of the isobaric C_{44} with temperature. The remaining decrease of the isobaric elastic constants with temperature, approximately 1/3 for C' and 1/2 for C_{44} , is then due to the explicit volume dependence of the elastic constants. Therefore, the explicit temperature dependence of the shear constants plays a major role in the variation of the isobaric shear constants with temperature.

The isochoric shear constants were then calculated at the volume, V' , of the solvent at the temperature at which the measurements were made. The results of this calculation are listed in Table 9; and, by inspecting these results, it can be seen that the net changes in these isochoric elastic constants with solute concentration are independent of temperature within the limits of experimental uncertainty. This was also shown to be the case for the directly measured isobaric shear constants. Therefore, the dependence of the isochoric and isobaric shear constants C' and C_{44} at only 297°K and 77°K on solute concentration is shown in Figures 9 and 10. Both the isochoric and isobaric shear constants increase with solute concentration, C_{44} linearly and C' with a slight curvature. The pure solute concentration dependence of the elastic constants represents approximately 50 per cent of the increase of the isobaric C' with solute concentration and approximately 25 per

TABLE 9. The isochoric elastic constants at the volume of the solvent, V' , at the temperature at which the measurements were made. The 0°K values were extrapolated from the higher temperature values and all elastic constants are in units of 10^{12} dyn/cm².

Isochoric Elastic Constant	Temperature	Concentration in At. % Nickel			
		0.0	3.02	6.02	9.73
$C' (V')$	297°K	0.2342	0.238	0.240	0.242
	195°K	0.2447	0.249	0.251	0.252
	77°K	0.2561	0.260	0.262	0.264
	0°K	0.257	0.261	0.263	0.265
$C_{44} (V')$	297°K	0.7556	0.759	0.765	0.767
	195°K	0.7816	0.786	0.791	0.793
	77°K	0.8086	0.814	0.818	0.820
	0°K	0.812	0.817	0.821	0.824
$B_S (V')$	297°K	1.3838	1.368	1.362	1.353
	195°K	1.4053	1.392	1.387	1.377
	77°K	1.4268	1.414	1.408	1.396
	0°K	1.429	1.417	1.412	1.400
$B_T (V')$	297°K	1.3437	1.428	1.322	1.313
	195°K	1.3807	1.368	1.362	1.353
	77°K	1.4212	1.408	1.403	1.391
	0°K	1.429	1.417	1.412	1.400

FIGURE 9. The isobaric shear constant $C'(P=0)$ and the isochoric shear constant $C'(V')$ at the volume, V' , of the solvent at 297°K and 77°K as a function of solute concentration.

FIGURE 10. The isobaric shear constant $C_{44}(P=0)$ and the isochoric constant $C_{44}(V')$ at the volume, V' , of the solvent at 297°K and 77°K as a function of solute concentration.

cent of the increase in the isobaric C_{44} with solute concentration. The remaining increase in the isobaric shear constants, 50 per cent for C' and 75 per cent for C_{44} , is then due to the volume dependence of the shear constants. This volume dependence of the elastic constants therefore accounts for the majority of the increase of the isobaric shear constants with solute concentration.

Bulk Modulus

The isochoric B_S and B_T were calculated at the volume, V'' , of the alloy at $0^\circ K$; and, the results of this calculation are listed in Table 8. Just as the shear constants are, the net changes in both the isochoric and isobaric bulk moduli with temperature are independent of solute concentration within the limits of experimental uncertainty. The dependence of both the isobaric and isochoric B_S and B_T on temperature for pure copper and the 9.73 atomic per cent nickel alloy is shown in Figures 11 and 12. Both the isobaric B_S and B_T decrease as the temperature is increased which is identical to the behavior of the isobaric shear constants. The isochoric B_T shows only a slight decrease with temperature which makes its explicit temperature dependence small; while, the isochoric B_S shows a large increase with temperature. This is completely opposite to the behavior of the explicit temperature dependence of the shear constants. The volume dependence is responsible for almost the entire variation with temperature of the isobaric B_T while it is responsible for the majority of the observed change in the isobaric B_S . This is again opposite to the behavior of the shear constants.

FIGURE 11. The isobaric elastic constant $B_S(P=0)$ and the isochoric elastic constant $B_S(V'')$ at the volume, V'' , of the crystal at 0°K as a function of temperature for copper and the 9.73 at. % Ni alloy.

FIGURE 12. The isobaric elastic constant $B_T(P=0)$ and the isochoric elastic constant $B_T(V'')$ at the volume, V'' , of the crystal at 0°K as a function of temperature for copper and the 9.73 at. % Ni alloy.

The isochoric B_S and B_T were calculated at the volume, V' , of the solvent at which the measurements were made. The results of this calculation are listed in Table 9. Both the net changes in the isobaric and isochoric bulk moduli with solute concentration are, just as the shear constants are, independent of temperature within the limits of experimental uncertainty. The dependence of both the isochoric and isobaric bulk moduli on solute concentration at 297° and 77°K is shown in Figures 13 and 14. Both the isochoric and isobaric bulk moduli appear to vary linearly with solute concentration; but, the isobaric bulk moduli increase with solute concentration while the isochoric bulk moduli decrease with solute concentration. The pure solute concentration dependent change represents approximately -90 per cent of the total change for both bulk moduli while the volume dependence accounts for approximately 190 per cent of the total change. Just as with the shear constants, the volume dependence accounts for most of the observed variation of the isobaric bulk moduli with solute concentration. However, the pure solute concentration dependence of the bulk moduli produces a decrease in these elastic constants while the pure solute concentration dependence produces an increase in the shear constants with solute concentration.

Discussion

The volume dependence of the elastic constants is related to the pressure derivatives of the elastic constants thru Eq. 13. Since all the pressure derivatives of the elastic constants are

FIGURE 13. The isobaric elastic constant $B_S(P=0)$ and the isochoric elastic constant $B_S(V')$ at the volume, V' , of the solvent at 297°K and 77°K as a function of solute concentration.

FIGURE 14. The isobaric elastic constant $B_T(P=0)$ and the isochoric elastic constant $B_T(V')$ at the volume, V' , of the solvent at 297°K and 77°K as a function of solute concentration.

positive, the volume dependence produces an increase in all the elastic constants as the volume is decreased at constant temperature and solute concentration. Therefore, the anharmonic nature of the crystal's internal energy which determines this volume dependence produces the same trend in all of the elastic constants.

However, the anharmonic character of the crystal's internal energy which determines the explicit temperature dependence of the elastic constants has a different effect on the elastic constants corresponding to a shear deformation than it does on those corresponding to a compressional deformation. The explicit temperature dependence of the shear constants produces a decrease with increasing temperature; however, for the isothermal bulk modulus, the explicit temperature dependence is almost zero while it produces an increase in the adiabatic bulk modulus with temperature.

The pure solute concentration dependence of the elastic constants also has a different effect on the elastic constants corresponding to shear deformations than it does on those corresponding to compressional deformations. This solute concentration dependence which arises solely from the addition of the solute altering the crystal's internal energy produces an increase in the shear constants with solute concentration at constant temperature and volume and a decrease in the bulk moduli with solute concentration at constant temperature and volume. The pure solute concentration dependence of both bulk moduli behave in the same manner and does not exhibit the anomalous behavior the explicit temperature dependence does.

The analysis of the elastic constants thus far has been quite involved; but, one trend was exhibited by all the elastic constants which can greatly simplify the description of these elastic constants. As far as one can ascertain from the experimental precision the net changes in both the isobaric and isochoric elastic constants with temperature are independent of solute concentration; and, the net changes in both the isobaric and isochoric elastic constants with solute concentration are independent of temperature. Therefore, this leads to the empirical conclusion that the elastic constants of this alloy system can be expressed as the elastic constants of the solvent plus an additive term, C^* , which is solely a function of solute concentration. This gives

$$C(T,V,n) = C(T,V,0) + C^*(n) \quad (16)$$

This C^* is independent of both temperature and volume. If the solute concentration dependence of the elastic constants can be explained at one temperature, then this should be the dominant contribution for all temperatures. Similarly, one needs only the volume and explicit temperature dependence of the solvent to explain these dependencies for the alloys.

Debye Temperature

At low temperatures where the lattice contribution to the specific heat is proportional to T^3 , the Debye anisotropic non-dispersive continuum model is valid for the lattice contribution to the heat capacity. By using this model, the lattice contribution to the heat capacity can be evaluated by summing the heat capacities of all the normal modes of the continuum. The change in the Debye temperature due to alloying follows from the change in the normal mode frequencies which can be determined from the elastic constant measurements.

The normal modes for the continuum are determined from the equation of motion of the system. Since the continuum model is anisotropic, the equation of motion will be a complicated function of the three independent elastic constants and the density. To initially avoid the mathematical complexity in order to obtain a physical description of these normal modes and just how they will be affected by alloying, only a longitudinal wave propagating in the x direction will be considered. The equation of motion for this specific mode is

$$\rho \frac{\partial^2 u}{\partial t^2} = C \frac{\partial^2 u}{\partial x^2} \quad (17)$$

where u is the displacement of the continuum from its equilibrium position in the x direction and C is the appropriate elastic constant for this mode. The solution to this equation is a plane wave

$$u(x,t) = A e^{i(\omega_j t - k_j x)} \quad (18)$$

where

$$\frac{\omega_j}{k_j} = v = \sqrt{\frac{C}{\rho}} \quad (19)$$

and ω_j is the normal mode frequency corresponding to the wave vector k_j , v is the sound velocity, and A is the amplitude of the wave. Now, $u(x,t)$ is subject to the normal periodic boundary conditions such that $u(x+L,t) = u(x,t)$ where L is a representative crystal length. This restricts k_j to integer values of $\frac{2\pi}{L}$. The sound velocity is constant for all k_j and is therefore non-dispersive. However, the number of normal modes possible is limited to the number of degrees of freedom of the atoms composing the solid which gives $3N$ normal modes for N atoms contained in volume L^3 .

The amount of thermal energy contained in the excitation of a normal mode of frequency, ω_j , is quantized and is some integer number of phonons, n_j , of energy $\hbar\omega_j$. The total thermal energy for the crystal lattice, excluding the zero point energy, simply becomes $\sum_j n_j \hbar\omega_j$. These phonon occupation numbers, n_j , are determined statistically from the Bose-Einstein distribution function given by

$$\langle n_j \rangle = \frac{1}{\frac{\hbar\omega_j}{k_B T} - 1} \quad (20)$$

where k_B is Boltzman's constant and $\hbar$ is Plank's constant divided

by 2π . At low temperatures, only long wavelength phonons can be excited and these phonons lie in the non-dispersive region of the crystal's actual dispersion relation.

The heat capacity, c_j , of the j^{th} mode can now be expressed as

$$c_j = \frac{\partial}{\partial T} \left(\frac{\frac{N\omega_j}{k_B T}}{e^{\frac{N\omega_j}{k_B T}} - 1} \right)_{V,n} \quad (21)$$

In the spirit of the quasi-harmonic approximation, it will be assumed that all ω_j 's are explicitly independent of temperature. By performing the indicated differentiation of the above expression under this assumption, the heat capacity becomes

$$c_j = k_B \frac{\frac{N^2 \omega_j^2}{k_B^2 T^2}}{\left(\frac{N\omega_j}{k_B T} \right)^2} \frac{e^{\frac{N\omega_j}{k_B T}}}{\left(e^{\frac{N\omega_j}{k_B T}} - 1 \right)^2} \quad (22)$$

The lattice contribution to the specific heat at constant volume, C_V , can now be expressed as

$$C_V = \sum_j c_j \quad (23)$$

At low temperatures where this non-dispersive continuum model is valid, C_V is related to the Debye temperature, Θ_D , by the Debye T^3 law which is

$$C_V \propto \left(\frac{T}{\Theta_D} \right)^3 \quad (24)$$

The dependence of the Einstein heat capacity, c_j , of the j^{th} mode on ω_j is shown in Figure 15. The heat capacity decreases with increasing ω_j , slowly at first and then as a pure exponential. Since, C_V is a sum of all c_j , C_V will decrease if the normal mode frequencies increase; and, from the Debye T^3 law, this increase in the normal mode frequencies will produce an increase in the Debye temperature.

The variation of the normal mode frequencies with solute concentration at fixed volume and temperature is derived below in terms of the experimentally measured quantities. In the non-dispersive region the dispersion relation is given simply by

$$\omega_j = v_j(\theta, \phi) k_j \quad (25)$$

where $v_j(\theta, \phi)$ is the velocity of sound in the direction θ, ϕ and k_j is the wave vector for the j^{th} mode and can be expressed by

$$k_j = \frac{2\pi}{L} \ell_j \quad (26)$$

where ℓ_j is a fixed number and L is a representative crystal length. Upon alloying, the velocity will change and the crystal will change dimensions which will influence the wave vector. However, because the crystal remains cubic in structure the direction θ, ϕ of the j^{th} mode will not be altered. If we consider the alloying to take place at fixed volume then the only changes in the normal mode frequencies arise because of the changes in velocity. We express this by taking the derivative

$$\left(\frac{\partial \ln \omega_j}{\partial \eta} \right)_{V,T} = \left(\frac{\partial \ln v_j(\theta, \phi)}{\partial \eta} \right)_{V,T} \quad (27)$$

FIGURE 15. The Einstein heat capacity, c_j , of the j^{th} normal mode as a function of that normal mode's frequency, ω_j .

This derivative can be related to the reported data thru

$$C_j = \rho v_j^2 \quad (28)$$

where C_j is the effective elastic constant for the j^{th} acoustic wave. Thus we obtain,

$$\left(\frac{\partial \ln v_j}{\partial n} \right)_{V,T} = \frac{1}{2} \left[\left(\frac{\partial \ln C_j}{\partial n} \right)_{V,T} - \frac{d \ln m}{dn} \right] \quad (29)$$

where m is the average molar mass of the alloy. For the copper-nickel alloys the second term in the above expression is positive while the first term is predominantly positive for the shear waves and negative for the longitudinal waves. Because the shear waves have low velocity, they dominate the behavior of the low temperature Θ_D and thus we expect Θ_D to increase with solute concentration at fixed T and V .

The variation of the normal mode frequencies with solute concentration at fixed T and P is easily understood by expressing ω_j as

$$\omega_j = 2\pi \lambda_j \sqrt{\frac{V^{1/3} C_j}{m}} \quad (30)$$

where V is the molar volume. The elastic constants all increase with solute concentration at fixed T and P while the average molar mass decreases. Both of these effects produce an increase in ω_j with solute concentration. However, $V^{1/3}$ decreases with increasing solute concentration; but, this effect is roughly an order of magnitude less than the effect produced by the variation of the

elastic constants with solute concentration. Therefore, the ω_j 's must increase with solute concentration thereby producing an increase in the Debye temperature with solute concentration at fixed T and P.

For the Debye anisotropic non-dispersive continuum model, the Debye temperature in the low temperature limit is given by

$$\Theta_D = \frac{h}{k_B} \left(\frac{3N_0}{4\pi V} \right)^{1/3} \left(\frac{1}{v^3} \right)^{-1/3} \quad (31)$$

where h is Plank's constant, N_0 is Avagadro's number, and $\left(\frac{1}{v^3} \right)^{-1/3}$ is the inverse cube root of the average inverse cubed wave velocity where the average is over the directions in the crystal.

Since the elastic constants are equal to the density times the velocity squared, the elastic constants at 0°K are then a measure of $\left(\frac{1}{v^3} \right)^{-1/3}$. It will be beneficial here to introduce a fictitious elastic constant, $\bar{C}$, such that

$$\bar{C} = \rho \left[\left(\frac{1}{v^3} \right)^{-1/3} \right]^2 \quad (32)$$

Although $\bar{C}$ has no real physical significance, it will be useful in the discussion of Rayne's⁹ "reduced" Debye temperature when the microscopic interpretation of the alloys is discussed. To calculate this $\bar{C}$, the following relation was used

$$\bar{C}^{-3/2} = \frac{\sum_{j=1}^3 \int C_j^{-3/2} d\Omega}{3 \int d\Omega} \quad (33)$$

where the C_i are the "elastic constants" associated with one quasi-longitudinal and two quasi-shear waves. The range of the integration is over the whole solid angle; but, for cubic crystals, symmetry permits the integration to be done over only 1/48 of the solid angle.

Now, the Debye temperature may be restated in terms of this fictitious elastic constant, $\bar{C}$, as

$$\theta_D = \frac{h}{k_B} \left(\frac{3N_o}{4\pi V} \right)^{1/3} \frac{\bar{C}^{1/2}}{\rho^{1/2}} \quad (34)$$

or terms of the average molar mass of the alloy as

$$\theta_D = \frac{h}{k_B} \left(\frac{3N_o}{4\pi} \right)^{1/3} \sqrt{\frac{V^{1/3} \bar{C}}{m}} \quad (35)$$

The pure solute concentration dependence of the Debye temperature can then be determined by holding the molar volume and mass fixed at those of the solvent and by using the isochoric 0°K elastic constants in the above expression to calculate the Debye temperature. This Debye temperature will be designated by θ_D^n . The changes in this Debye temperature with solute concentration are then due only to the addition of the solute altering the crystal's internal energy by changing the band structure and ion-ion repulsive interaction.

The dependence of the Debye temperature on the average mass can then be determined by holding the volume and elastic constants fixed at those of the solvent and varying the mass. This Debye temperature will be designated by θ_D^m . The variation of this Debye temperature with solute concentration is merely due to the change in mass

altering the kinetic energy portion of the equation of motion of the continuum and is independent of the internal energy of the crystal.

The calculation of the integrals used in the calculation of the Debye temperature were performed with a computer program written by D.E. Schuele and C.S. Smith.⁴⁹

The limiting value of the isobaric Debye temperature was calculated for copper and the copper-nickel alloys from the extrapolated 0°K elastic constants. These Debye temperatures are listed in Table 10; and their uncertainty due to the experimental uncertainty of the elastic constants was estimated to be 0.5 per cent. The calorimetric value of the Debye temperature for pure copper is $344.5 \pm 1.5^\circ\text{K}$ ³⁴ which is in excellent agreement with the value calculated from the elastic constants of $344.1 \pm 1.7^\circ\text{K}$. The isobaric Debye temperature's dependence on solute concentration is shown in Figure 16. The least squares fit through the calculated points agrees fairly well with the linear extrapolation to the Debye temperature of pure nickel of 440°K .⁵⁰ The isobaric Debye temperature increases with solute concentration as expected from the analysis of the dependence of the normal mode frequencies at fixed T and P on solute concentration.

The Debye temperatures θ_D^n and θ_D^m were calculated as outlined above and the results of this calculation are listed in Table 10. The dependence of these Debye temperatures on solute concentration is also shown in Figure 16 along with the dependence of the isobaric Debye temperature on solute concentration. Both θ_D^n and θ_D^m increase with solute concentration as predicted from the discussion

TABLE 10. The isobaric Debye temperature calculated from the extrapolated 0°K elastic constants by using the Debye non-dispersive continuum model; the pure solute concentration dependent Debye temperature, Θ_D^n ; and, the mass dependent Debye temperature, Θ_D^m for copper and the copper-nickel alloys.

Nickel Concentration (At. % Ni)	Θ_D	Θ_D^n	Θ_D^m
0.0	344.1	344.1	344.1
3.02	347.6	345.6	344.5
6.02	350.7	346.8	344.9
9.73	353.9	347.5	345.4

FIGURE 16. The isobaric Debye temperature, θ_D ; the pure solute concentration dependent Debye temperature, θ_D^η ; and, the mass dependent Debye temperature, θ_D^m , as a function of solute concentration.

of the dependence of the normal modes on pure solute concentration and mass. The variation of the Debye temperature θ_D^n on solute concentration represents the change in the Debye temperature produced by the addition of the solute altering the crystal's internal energy by changing the band structure and ion-ion repulsive interaction; and, this variation is roughly one third of the total change. The change due to the mass dependence of the Debye temperature which is produced by the addition of a solute of a different mass altering the kinetic energy portion of the equations of motion of the continuum represents only 13 per cent of the total change. The remaining change is due to the volume dependence of the Debye temperature and represents over one-half the observed change.

Grüneisen Parameter

The pressure derivatives of the elastic constants and the thermal expansion results from the anharmonic character of the crystal's internal energy. The Grüneisen parameter is a measure of the anharmonic character of the crystal and may be calculated either from thermodynamic data or from the pressure derivatives of the elastic constants.

The anharmonic character of the crystal's internal energy is related to the volume dependence of the normal mode frequencies of the lattice. This volume dependence is described by a mode gamma, γ_j , defined by

$$\gamma_j = - \left(\frac{\partial \ln \omega_j}{\partial \ln V} \right)_{T, \eta} \quad (36)$$

where ω_j is the frequency of the j^{th} normal mode, and V is the crystal volume. It was shown before that ω_j can be expressed in terms of the crystal volume and appropriate elastic constant by the expression

$$\omega_j = 2\pi \ell_j \sqrt{\frac{V^{1/3} C_j}{m}} \quad (30)$$

where C_j is the elastic constant which describes the wave velocity for the given direction and branch in the Brillouin zone corresponding to the j^{th} normal mode. Therefore, all the non-dispersive low frequency modes for a given branch and direction in the Brillouin zone have the same mode gamma given by

$$\gamma_j = - \frac{1}{6} - \frac{1}{2} \left(\frac{\partial \ln C_j}{\partial \ln V} \right)_{T, \eta} \quad (37)$$

or

$$\gamma_j = - \frac{1}{6} + \frac{1}{2} \frac{B_T}{C_j} \left(\frac{\partial C_j}{\partial P} \right)_{T, \eta} \quad (38)$$

From the cubic symmetry of this alloy system, it is possible to calculate all the low frequency mode gammas for each direction in the Brillouin zone from the elastic properties measured in the [110] direction.

The low frequency mode gammas for the three major crystallographic directions calculated from the above equation are listed in

Table 11. The uncertainty in these gammas due to the experimental uncertainty in the elastic constants and their pressure derivatives is estimated to be 2.5 per cent. All the mode gammas show a slight decrease with temperature. The largest decrease is exhibited by the mode gamma for C' which shows a 5.5 per cent decrease; but, the remaining mode gammas show a nominal decrease of only 2 per cent. The variation of these mode gammas at fixed P and n with temperature is due to both the volume dependence and explicit temperature dependence of the elastic constants and their pressure derivatives. The explicit temperature dependence of the elastic constants has already been determined; but, to determine the explicit temperature dependence of the pressure derivatives, the higher order pressure derivatives must be known. Since these higher order pressure derivatives could not be observed experimentally, the explicit temperature dependence of these mode gammas cannot be separated from their volume dependence. However the experimental uncertainty in these mode gammas is 2.5 per cent; and, the decrease of the mode gammas with temperature is within the limits of experimental uncertainty with the exception of the C' mode gamma. Thus as far as the experimental measurements indicate, there might be a slight decrease in the mode gammas with temperature; but, it cannot be resolved experimentally. Since this decrease is slight and since the explicit temperature dependence of the mode gammas cannot be separated from their volume dependence, the explicit temperature dependence of the mode gammas will be considered to be small and will be neglected.

Also within the limits of experimental uncertainty, all of the

TABLE 11. The low frequency mode gammas of copper and copper-nickel alloys for the three major crystallographic directions. The 0°K values were calculated from the extrapolated elastic constants and pressure derivatives.

Gamma and Mode	Temperature	Concentration in At. % Ni.			
		0.0	3.02	6.02	9.73
$\gamma(C_{11})$ [100] Long.	297°K	2.29	2.31	2.28	2.29
	195°K	2.18	2.22	2.20	2.26
	77°K	2.24	2.23	2.21	2.23
	0°K	2.25	2.24	2.21	2.22
$\gamma(C_{44})$ [100] Trans.	297°K	1.91	1.88	1.89	1.88
	195°K	1.86	1.85	1.86	1.85
	77°K	1.87	1.83	1.82	1.84
	0°K	1.88	1.84	1.82	1.84
$\gamma(C'_{11})$ [110] Long.	297°K	2.25	2.26	2.24	2.24
	195°K	2.15	2.18	2.17	2.21
	77°K	2.20	2.19	2.17	2.19
	0°K	2.21	2.19	2.17	2.19
$\gamma(C')$ [110] Trans.	297°K	1.43	1.46	1.45	1.43
	195°K	1.37	1.40	1.39	1.41
	77°K	1.41	1.38	1.37	1.36
	0°K	1.41	1.38	1.37	1.36
$\gamma(C_{44})$ [110] Trans.	297°K	1.91	1.88	1.89	1.88
	195°K	1.86	1.85	1.86	1.85
	77°K	1.87	1.83	1.82	1.84
	0°K	1.88	1.84	1.82	1.84
$\gamma(C_{\ell})$ [111] Long.	297°K	2.24	2.24	2.23	2.23
	195°K	2.15	2.17	2.16	2.20
	77°K	2.20	2.18	2.16	2.18
	0°K	2.20	2.18	2.16	2.18
$\gamma(C_t)$ [111] Trans.	297°K	1.72	1.72	1.72	1.71
	195°K	1.67	1.68	1.68	1.68
	77°K	1.69	1.66	1.65	1.65
	0°K	1.69	1.66	1.65	1.65

mode gammas show no significant change with solute concentration. This is merely a reflection of the conclusion which was reached earlier that the elastic constants of the alloys can be represented by the elastic constants of the solvent plus an additive term, C^* , which is only dependent on solute concentration. This conclusion was reached by using the fact that the volume dependence of the elastic constants at fixed T and n , as determined from the pressure derivatives of the elastic constants, was not measurably affected by changes in either temperature or solute concentration. The insensitivity of the mode gammas to solute concentration at all temperatures is then only another way to restate this previous observation.

In the spirit of the quasi-harmonic approximation, it will be assumed that the explicit temperature dependence of the normal mode frequencies is zero. Under this assumption, the macroscopic Grüneisen parameter, γ_G , is defined as

$$\gamma_G = \frac{3\alpha V B_s}{C_p} \quad (39)$$

From the Mie-Grüneisen equation of state one can show that this is a weighted average of the individual mode gammas such for a crystal of N atoms

$$\gamma_G = \frac{\sum_j \gamma_j c_j}{\sum_j c_j} \quad (40)$$

where the summation is over the $3N$ normal modes and the weighting factor, c_j , is the Einstein heat capacity of the j^{th} mode. This model predicts an explicit temperature dependence of the Grüneisen

parameter through the explicit temperature dependence of the weighting factors.

In the limit of high temperature where all modes are excited and all c_j are equal, γ_G simply becomes the average of the $3N$ mode gammas. This limit can be estimated from the elastic constant data if it is assumed that the mode gammas in the dispersive region are the same as those in the non-dispersive region and that the Brillouin zone is spherical thus giving the same number of modes in each direction. This estimated value is designated by $\bar{\gamma}_H$. At low temperatures, only the low frequency modes are excited and the Debye non-dispersive continuum model is valid. The number of modes in the j^{th} direction is then proportional to v_j^{-3} where v_j is the velocity in the j^{th} direction. Thus the weighting factor is just v_j^{-3} . This calculated value is designated by $\bar{\gamma}_L$.

The Grüneisen parameters, $\bar{\gamma}_L$ and $\bar{\gamma}_H$, were calculated from the elastic constants and their pressure derivatives; and, the Grüneisen parameter, γ_G , was calculated from the data listed in Table 2. The results of these calculations are listed in Table 12. The uncertainty in $\bar{\gamma}_L$ and $\bar{\gamma}_H$ due to the experimental uncertainty in the elastic constants and their pressure derivatives is estimated to be 3 per cent while the uncertainty in γ_G , due mainly to the uncertainty in the thermal expansion data, is estimated to be 2 per cent for pure copper and 5 per cent for the alloys. First, $\bar{\gamma}_L$ and $\bar{\gamma}_H$ for pure copper will be compared with the results of γ_G that were calculated from the thermal expansion data by Carr, McCammon, and White.³³ The temperature dependence of these γ_G is shown in

TABLE 12. The Grüneisen parameters, $\bar{\gamma}_L$ and $\bar{\gamma}_H$, calculated from the elasticity data and the Grüneisen parameter, γ_G , calculated from the thermal expansion data..

Gamma Temperature		Concentration in At. % Ni.			
		0.0	3.02	6.02	9.73
$\bar{\gamma}_L$	297°K	1.73	1.73	1.73	1.72
	195°K	1.67	1.69	1.69	1.69
	77°K	1.70	1.67	1.66	1.66
	0°K	1.71	1.67	1.66	1.66
$\bar{\gamma}_H$	297°K	1.94	1.95	1.93	1.92
γ_G	297°K	2.01	2.00	2.00	2.00
	195°K	2.01	1.99	1.99	1.97
	77°K	1.95	1.93	1.95	1.96
	0°K	1.72*			

* Limiting value of γ_G calculated by Carr, McCammon, and White, ref. 33.

FIGURE 17. The Gruneisen parameter, γ_G , calculated from thermal data³³ as a function of temperature and the high and low temperature limiting values, $\bar{\gamma}_H$ and $\bar{\gamma}_L$, calculated from the present elastic data for pure copper.

Figure 17 along with the limiting value of $\bar{\gamma}_L$ and $\bar{\gamma}_H$ for pure copper. The γ_G show an increase with temperature which is the observed trend of most materials and is due primarily to the temperature dependence of the Einstein heat capacities of the normal modes at fixed P and n . The limiting value of γ_G of $1.72 \pm .03$ ³³ is in excellent agreement with the limiting value of $\bar{\gamma}_L$ of $1.71 \pm .05$. The value of $\bar{\gamma}_H$ is slightly lower than the corresponding value of γ_G which is probable due to the approximations which were necessary in the calculation of $\bar{\gamma}_H$.

Within the limits of experimental uncertainty, $\bar{\gamma}_L$ shows no significant change with solute concentration. Since $\bar{\gamma}_L$ is an average of the low frequency mode gammas, $\bar{\gamma}_L$ must be insensitive to solute concentration since the low frequency mode gammas are. The Grüneisen parameters $\bar{\gamma}_L$ and $\bar{\gamma}_H$ also show no significant change with solute concentration within the limits of experimental uncertainty which merely means that the temperature dependence of the Grüneisen parameter for the alloys is the same as that of the solvent. These Grüneisen parameter are at fixed P and n instead of the desired V and n . Thus the variation of these Grüneisen parameters with temperature at fixed P and n is dependent on both the volume dependence and explicit temperature dependence of the Einstein heat capacity of the normal modes. The volume dependence of the c_j enters in through the volume dependence of the ω_j of which the low frequency mode gammas are a direct measure. The explicit temperature dependence of the c_j in this model is implicitly given by equation 22. Since the volume dependence of the low frequency normal modes

is insensitive to solute concentration, it is not surprising that the γ_G of the alloys have the same temperature dependence of the γ_G of the solvent.

The quasi-harmonic approximation which was used to calculate the Grüneisen parameter is based on the assumption that the ω_j are independent of temperature. At fixed V and n , the shear constants exhibit a significant explicit temperature dependence which makes ω_j dependent on temperature. For example, the explicit temperature dependent change of C' from 297°K to 0°K is roughly 8 per cent which, from equation 30, produces a 4 per cent change in the normal mode frequency corresponding to this shear wave. The effect of the temperature dependence of ω_j on the Einstein heat capacity is that the implicit temperature dependence of c_j given by equation 21 overpowers the explicit temperature dependence of c_j resulting from the temperature dependence of ω_j to a point where it may be neglected. Therefore, this model is an adequate approximation for the discussion of the anharmonic properties of this alloy system via the Grüneisen parameter.

Equation of State

Anderson⁴⁸ has shown that the isothermal bulk modulus and its pressure derivative, measured at low pressure, can be used through the Murnaghan equation of state to predict the compression of solids at high pressure. To obtain this empirical equation of state, the isothermal bulk modulus is first expanded in a Taylor series at fixed T and n about the pressure at which the isothermal bulk modulus was

measured. This series is

$$B_T(T, P, \eta) = B_T(T, P_0, \eta) + \left(\frac{\partial B_T}{\partial P} \right)_{T, \eta} (P - P_0) \quad (41)$$

or

$$-V \left(\frac{\partial V}{\partial P} \right)_{T, \eta} = B_T(T, P_0, \eta) + \left(\frac{\partial B_T}{\partial P} \right)_{T, \eta} (P - P_0) \quad (42)$$

The termination of this series is made after the linear term since, as mentioned before, the higher order derivatives of the elastic constants with respect to pressure could not be observed experimentally and are therefore assumed to be negligible. The Murnaghan logarithmic equation of state is then obtained by integrating this expression which yields

$$\ln \left(\frac{V}{V_0} \right) = - \frac{1}{\left(\frac{\partial B_T}{\partial P} \right)_{T, \eta}} \ln \left[\left(\frac{\partial B_T}{\partial P} \right)_{T, \eta} \frac{P}{B_T(T, P_0, \eta)} + 1 \right] \quad (43)$$

where P_0 has been set equal to zero and V_0 is the zero pressure volume.

To test the validity of the Murnaghan equation, a plot of this equation in reduced form for pure copper at 297°K is shown in Figure 18 along with the room temperature shock wave data of McQueen and Marsh⁵¹ for pure copper which extends to $P/B_T = 1.12$ which is equivalent to a pressure of 1.5 megabar. The Murnaghan equation is in excellent agreement with the results of the shock wave measurements up to $B/B_T \approx 0.4$ which corresponds to approximately 190 times

FIGURE 18. The compression of pure copper at room temperature from the shock wave data of McQueen and Marsh⁵¹ and as predicted from the ultrasonic data.

the maximum pressure used in this experiment. The agreement of the Murnaghan equation with the shock wave data up to this pressure undoubtedly shows the usefulness of this equation in the extrapolation of the equation of state of copper to higher pressures. The disagreement of the Murnaghan equation with the shock wave data above this pressure is probably due to the higher order pressure derivatives of the isothermal bulk modulus which could not be detected in the pressure range of 2.64 kbar used in this experiment. An estimate of the second derivative of the isothermal bulk modulus with respect to pressure can be made by using the second order Murnaghan equation which Loje and Schuele⁵² developed by extending the Taylor series to the second derivative and then integrating this series. By using this derivative as a variable to fit the second order Murnaghan equation to the shock wave data at 1.5 megabar, this second derivative was estimated to be $-0.0011 \text{ kbar}^{-1}$. A plot of this second order Murnaghan equation is also shown in Figure 18 along with the first order Murnaghan equation and the shock wave data. The agreement of the second order Murnaghan equation with the shock wave data is excellent which tends to indicate that the exclusion of second derivative of the isothermal bulk modulus with respect to pressure is the reason for the disagreement of the first order Murnaghan equation at high pressures. In the pressure range of 2.64 kbar used in this experiment, the effect of this second derivative would only be -0.03 per cent of the total effect of the first derivative. Since the precision of the pressure derivatives is at best one per cent for a directly measured wave, this second derivative could not be observed.

As it was shown previously, the pressure derivative of the isothermal bulk modulus shows no change with solute concentration within the limits of experimental uncertainty. The plot of the Murnaghan equation in this reduced form can then be used to extrapolate the equation of state of the alloys to higher pressures at this temperature of 297°K. If the pressure derivative of the isothermal bulk modulus were independent of temperature, then this plot could also be valid for all temperatures; however, the pressure derivative of the isothermal bulk modulus exhibits a 6 per cent decrease from 297°K to 0°K. This 6 per cent decrease in the pressure derivative only produces a 0.4 per cent change in the compression at $P/B_T = 0.4$ at which this equation begins to disagree with the shock wave data. Since the Murnaghan equation is relatively insensitive to this small change in the pressure derivative, the plot of the Murnaghan equation in reduced form can be used in extrapolating the equation of state for all alloys at all temperatures.

MICROSCOPIC INTERPRETATION

The physical properties of copper and the copper-nickel alloys can be theoretically determined if the crystal's internal energy and its variation upon alloying is known. The crystal's internal energy is determined from the band structure of the conduction electrons and from the ion-ion core overlap. Both of these contributions are affected by the addition of the solute; but, the extent of their modification by the addition of the solute, as summarized in the Introduction, is still not clear. It will then be beneficial to draw correlations of the experimental results with parameters which are characteristic of either the band structure or the ion-ion core overlap in order to gain insight as to the extent of the modification of these contributions by the addition of the solute. Since any valid microscopic theory of the copper-nickel alloys should also be applicable to other noble metal alloys, these correlations will also be made with other noble metal alloys in order to obtain as much information as possible about the system before the details of the band structure and the ion-ion core overlap are discussed.

In order to provide a uniform basis for the following discussion, the rigid band model will be used to initially draw these correlations. To be consistent with this model, it will be assumed that the ion cores are identical and that there is no change in the ion-ion core overlap with solute concentration. Therefore, only correlations of the experimental results with the band structure of

the conduction electrons will be made. The changes in the band structure upon alloying can be described by the parameter q which is the ratio of the number of conduction electrons per atom. To draw correlations of a physical property with q , the dependence of this property on q for the copper-nickel alloys must also be compared with the dependence of this property on q for the other noble metal alloys. The only other low temperature measurements of the elastic constants of a copper alloy system were carried out by Rayne¹⁷ for the alpha phase copper-zinc alloys in the temperature range of 300°K. to 4.2°K. The results of Rayne's measurements for the copper-zinc alloys will then be used to make comparisons with the results for the copper-nickel alloys.

The rigid band model defines q for these alloy systems as follows: Nickel is given a valency of zero when alloyed with copper which results in a filled 3d ion core identical to that of pure copper such that $q = 1 - n/100$. Similarly, zinc is given a valency of two when alloyed with copper which results in an identical filled 3d ion core making $q = 1 + n/100$. Since almost all physical properties are measured at fixed P instead of fixed V , the rate of change of molar volume with q must also be taken into account. The molar volume increases linearly with q for both alloy systems; but, the rate of increase with q for the copper-zinc alloys is 2.0 times that of the copper-nickel alloys. Since the rate of change of molar volume with q is different for each alloy system, it would be physically meaningful to remove the volume dependence from the measured properties of the copper-zinc alloys as was done for the

copper-nickel alloys. This requires a knowledge of the pressure derivatives of the elastic constants of the copper-zinc alloys; but, these derivatives have not been measured. Rayne's¹⁷ measurements of the elastic constants of the copper-zinc alloys did show that the net changes in the measured isobaric elastic constants with solute concentration are independent of temperature which is precisely the same behavior as the elastic constants of the copper-nickel alloys. This indicates that the anharmonic character of the crystal's internal energy which produces the temperature dependence of the measured isobaric elastic constants is unaffected by the addition of the solute. It will then be assumed that the anharmonic character of the crystal's internal energy which affects the pressure derivatives of the elastic constants is also unaffected by the addition of the solute and that the pressure derivatives of the elastic constants of the copper-zinc alloys will then be the same as those of pure copper which is basically the experimental results for the copper-nickel alloys. Under this assumption, the volume independent elastic constants for the copper zinc alloys will be calculated; and, the volume independent results for both systems will be compared and correlations made with q .

First, correlations of Rayne's⁹ "reduced" Debye temperature and the pure solute concentration dependent Debye temperature will be made with q . The dependence of the elastic constants at both fixed P and fixed V on q will be presented; and, the relationship between the elastic constants and the Debye temperature will be discussed. Finally, the discrepancies of these results with the

rigid band model will be discussed in the light of other experimental properties and more recent theories.

Debye Temperature

John Rayne⁹ was the first to draw a correlation of a "reduced" Debye temperature with the electron per atom ratio, q , for this system. The "reduced" Debye temperature, Θ_r , is defined as

$$\Theta_r = \sqrt{\frac{m_n V_s^{1/3}}{m_s V_n^{1/3}}} \Theta_D(V_s, n) \quad (44)$$

where m_n and V_n are the average gram atomic weight and 0°K molar volume of the alloy and m_s and V_s are the gram atomic weight and 0°K molar volume of the solvent. By using the expression given by equation 35 for the Debye temperature, this "reduced" Debye temperature becomes

$$\Theta_r = \frac{h}{k_B} \left(\frac{3N_o}{4\pi} \right)^{1/3} \left(\frac{V_s^{1/3}}{m_s} \right)^{1/2} \sqrt{\bar{C}} ; \quad (45)$$

and, by neglecting the various constants, this reduces to

$$\Theta \propto \sqrt{\bar{C}} \quad (46)$$

Therefore, this "reduced" Debye temperature is dependent on only the fictitious elastic constant $\bar{C}$.

Rayne wanted to calculate the mass and volume independent Debye temperature as was done for the copper-nickel alloys; but, at this time, the low temperature pressure derivatives of the

elastic constants of copper and the copper-zinc alloys had not been measured. Therefore, Rayne was only able to remove the Debye temperature's explicit mass and volume dependence with this concept of the "reduced" Debye temperature.

The "reduced" Debye temperature was calculated for the copper-nickel alloys by using the present measurements and for the copper-zinc alloys by using Rayne's¹⁷ 4.2°K elastic constant measurements. The normalized "reduced" Debye temperature is linear in q as shown in Figure 19. The "reduced" Debye temperature is a function of the isobaric elastic constants which are dependent on both volume and solute concentration. As was previously shown, the volume dependence of the elastic constants of the copper-nickel alloys accounts for the majority of the variation of the isobaric elastic constants with solute concentration. Since the rate of change of molar volume is different for each alloy system, one might then expect a slope discontinuity in this plot at $q = 1.0$ due to the volume dependence of the elastic constants; but, this is not the case. Rayne⁹ concluded that this was only a reflection of the shear constants being dependent on q despite the differences in the rate of change of molar volume. He then showed that the room temperature shear constants of the copper alloys which had been measured at that time showed a linear dependence on q .

Before investigating the dependence of the elastic constants on q , the Debye temperature will be investigated further by calculating the true volume and mass independent Debye temperature. The mass and volume independent Debye temperature, Θ_D^n , was calculated

FIGURE 19. The normalized "reduced" Debye temperature as a function of the electron per atom ratio for the copper-nickel alloys and the copper-zinc alloys.

for the copper-zinc alloys under the assumption which was made earlier that the pressure derivatives of the elastic constants are unaffected by the addition of the solute. The dependence of the mass and volume independent Debye temperature for both alloy systems is shown in Figure 20. There is not only a discontinuity in the slope of this curve at $q = 1.0$; but, the slope changes sign. One must be cautious in attempting to interpret these curves because of the relatively small changes which are dealt with. However, it can safely be said that the data seems to indicate that the mass and volume independent Debye temperature appears to increase with solute concentration despite the fact that q increases with solute concentration for the copper-zinc alloys and decreases with solute concentration for the copper-nickel alloys. This last curve is of significance to the theorist since their calculations are for the most part carried out at fixed volume.

Although Rayne's "reduced" Debye temperature has no real physical significance, Collins¹⁹ later showed from the experimental results of other investigators that the somewhat linear dependence of the "reduced" Debye temperature on q is a basic characteristic of most noble metal alloys. However, it has just been shown that the true mass and volume independent Debye temperature for the copper-nickel alloys and the copper-zinc alloys does not exhibit this linear dependence on q . Since these Debye temperatures are functions of only the elastic constants, it would be much more advantageous to investigate the elastic constants themselves rather than the Debye temperature. If the elastic constants'

FIGURE 20. The mass and volume independent Debye temperature, Θ_D^n , as a function of the electron per atom ratio for the copper-nickel alloys and the copper-zinc alloys.

dependence on q can be interpreted properly, the interpretation of the dependence of the "reduced" Debye temperature and of the true mass and volume independent Debye temperature of q will readily follow.

Elastic Constants

Before the experimental results are presented as a function of q , a brief discussion of just how the crystal's internal energy contributes to the three independent elastic constants will be given.

When a crystal undergoes a shear deformation, the resulting redistribution of the ion cores alters the total electrostatic energy of the crystal. This change in energy produces what is normally termed the long range electrostatic contribution to the shear constants. Fuchs⁷ calculated this contribution for monovalent metals at 0°K; and, the results of his calculation for pure copper are 0.2596×10^{12} dyn/cm² for C_{44} and 0.0290×10^{12} dyn/cm² for C' . Upon alloying, the rigid band model predicts that these contributions will vary as q^2 if the volume is held fixed.

A shear deformation in real space also produces a shear deformation of the Brillouin zone in reciprocal space. If the Fermi surface is non-spherical, this deformation of the Brillouin zone alters the density of states of the conduction electrons making states of lower energy available. The electrons will then redistribute themselves to obtain this lower energy thereby reducing the total kinetic energy of the conduction electrons. This change in energy produces a negative contribution to the shear constants from the

Fermi energy. Collins¹⁹ calculated the contribution to the shear constants from the non-spherical Fermi surface of the noble metals; and, the results of his calculation for copper at 0°K are -0.425×10^{12} dyn/cm² for C_{44} and -0.075×10^{12} dyn/cm² for C' . The precise details of his calculation and the dependence of these contributions on q will be discussed when the experimental results for the elastic constants are presented as a function of q .

The short range ion-ion core overlap also contributes to the shear constants. The overlap of the ion cores produces a strong repulsive interaction resulting from the Pauli exclusion principle keeping like spins apart. This interaction accounts for the remaining contribution to the shear constants. Although Hafemeister⁸ calculated the Born-Mayer potential from an exchange charge model for the noble metals, a calculation of the noncentral force contribution to this interaction from first principles has not yet been done. It must also be pointed out that a different model is often necessary to describe this overlap when other physical properties are discussed. For example, the magnetic susceptibility is best described by a model for this overlap consisting of a continuous band of the d electrons. Ferromagnetism and large paramagnetism are accounted for in this model by having this d band contribute some of its electrons to the conduction band thereby making electrons available in this band to align their spins. Although the concept of the ion-ion core overlap best describes this contribution to the elastic constants, the band model must also be used when correlating susceptibility data with elasticity data. To be consistent with the

rigid band model, it will be assumed that the contribution to the shear constants from the repulsive interaction of the ion cores does not change with solute concentration.

The bulk modulus corresponds to a uniform compression; and, therefore, the bulk modulus depends on all the volume dependent terms in the crystal's internal energy. This includes the total electrostatic energy, the energy produced by the ion-ion core overlap, the correlation energy of the conduction electrons, the average kinetic energy of the conduction electrons, the exchange energy of the conduction electrons, and the zero point energy of the crystal. Since both the volume dependence of these terms and their variation with q must be known, the calculation of the bulk modulus and its dependence on q from these terms is extremely difficult. Therefore, the bulk modulus will only be discussed qualitatively.

Besides discussing the two shear constants and the bulk modulus, the elastic constant C'_{11} will also be discussed. The reason for this is that the Debye temperature is determined by considering the normal modes of the solid which are characterized by the two shear constants and the longitudinal constant C'_{11} . Since the effects of the deformation corresponding to C'_{11} are difficult to interpret, C'_{11} will only be discussed with regards to the Debye temperature.

The dependence of the normalized 0°K isobaric elastic constants C' , C_{44} , and C'_{11} on q for both alloy systems is shown in Figure 21. Both C' and C'_{11} appear fairly linear in q ; but,

FIGURE 21. The normalized isobaric elastic constants C'_{11} , C' , and C_{44} as a function of the electron per atom ratio for the copper-nickel alloys and the copper-zinc alloys.

C_{44} deviates slightly from linearity. If a straight line were drawn through the points for C_{44} , no point would be more than 1.5 per cent from line. The "reduced" Debye temperature is calculated from these elastic constants; and, their linearity in q is the reason why the "reduced" Debye temperature is linear in q which is the same observation made by Rayne.⁹ Again, one might expect a slope discontinuity at $q = 1.0$ since the volume dependence of the elastic constants accounts for the majority of their change with solute concentration and since the rate of change of molar volume with q is different for each alloy system.

The shear constants will now be investigated at constant volume; and, comparisons of the experimental results will be made with the results of Collins,¹⁹ calculation. The normalized isochoric shear constants at the volume of the solvent, V' , at 0°K are plotted as a function of q for both alloy systems in Figures 22 and 23. The isochoric C' decreases linearly with q ; while the isochoric C_{44} not only has a slope discontinuity at $q = 1.0$, but the slope changes sign.

Collins,¹⁹ model will be used to interpret these results since his model is based on rigid band formalism which is consistent with this discussion. This model consists of the long range electrostatic contribution as calculated by Fuchs,⁷ a contribution from the ion-ion repulsive interaction which is unaffected by the addition of the solute, and the contribution to the shear constants from the average Fermi energy which was calculated using an "8-6" cone model.

In order to properly interpret Collins' results, a brief dis-

FIGURE 22. The normalized isochoric elastic constant $C'(V')$ as a function of the electron per atom ratio for the copper-nickel alloys and the copper-zinc alloys. The results of Collins' calculation were sketched from the curves shown in reference 19; and, they therefore should be considered as a rough estimate of this calculation.

FIGURE 23. The normalized isochoric elastic constant $C_{44}(V')$ as a function of the electron per atom ratio for the copper-nickel alloys and the copper-zinc alloys. The results of Collins' calculation which were obtained from the curves given in reference 19 were scaled down by a factor of 1/5 in order to contain his results on this plot and then sketched in. These curves should be considered as only a rough estimate of this calculation.

cussion of the details of his calculation will be presented.

Collins' calculation is best understood by considering the effects of the shear deformations C_{44} and C' on the Brillouin zone. The Brillouin zone of an alpha phase metal consists of eight hexagonal $\{111\}$ faces and six square $\{200\}$ faces. The shear deformation C_{44} corresponds to a first order shift of the hexagonal $\{111\}$ faces and a second order shift of the square $\{200\}$ faces. The shear deformation C' corresponds to a first order shift of the square $\{200\}$ faces and a second order shift of the hexagonal $\{111\}$ faces. Since the Fermi surface of the noble metals makes contact with the $\{111\}$ faces of the Brillouin zone, the movement of the $\{111\}$ faces alters the density of states such that the area of contact to the Fermi surface with this face is altered which makes states of lower energy available to the conduction electrons thereby reducing the average Fermi energy. The Fermi surface does not contact the $\{200\}$ faces; and, therefore, the effect of the movement of the $\{200\}$ faces on the average Fermi energy is not as large as the effect of the movement of the $\{111\}$ faces. Since the movement of the $\{111\}$ faces is a first order effect for the shear deformation C_{44} , the contribution from the second order shifts of the $\{200\}$ faces is small and may be neglected.¹⁹ However, this contact of the Fermi surface with the $\{111\}$ faces produces a significant contribution from the second order shift of these faces for the shear deformation C' . To properly account for this, Collins' represented the Brillouin zone by eight cones based on the $\{111\}$ faces and six cones based on the $\{200\}$ faces

instead of the 8-cone model used by Ziman⁵³ to discuss the transport properties. Collins then fit the band gap across the {111} face, V_{111} , and the band gap across the {200} face, V_{200} , to make the constant energy surfaces of this model fit the experimental results of the neck radius and central belly radius of the Fermi surface of pure copper. He then assumed that V_{111} and V_{200} did not change upon alloying and were unaffected by a shear deformation.

The results of this calculation for C' are shown in Figure 23 along with the experimental results. The theoretical variation of C' with q is in fair agreement with the experimental results. The theoretical results for C_{44} are displayed in Figure 24 along with the experimental results. The theoretical curve was scaled down by a factor of 1/5 since this theoretical variation of C_{44} with q is much larger than what is observed experimentally. The theoretical curve for C_{44} shows a slope discontinuity at $q = 0.92$ at which point the slope changes sign. Above this q value, C_{44} increases linearly with q ; and, below this q value C_{44} increases with decreasing q . Although the magnitude of the variation of C_{44} with q as calculated by Collins is much larger than what is observed experimentally, the experimental results are basically in qualitative agreement with the theoretical results with the exception of the slope discontinuity not occurring at the same q value.

One difficulty in using the rigid band model to determine the dependence of C_{44} on q is that the rigid band model does not adequately describe the variation of the electronic contribution to the specific heat. Various measurements of the electronic contribu-

tion to the specific heat¹¹⁻¹⁶ of the noble metal alloys indicates that the area of contact of the Fermi surface with the $\{111\}$ face; and, consequently the density of states near this face is not properly determined by the rigid band model. (The term density of states is used in reference to only the density of states at the Fermi level). Collins predicts the slope discontinuity for C_{44} to occur at $q = 0.92$ instead of the observed discontinuity at $q = 1.0$. The prediction of this discontinuity to occur at $q = 0.92$ arises because there is a peak in the density of states curve at this q value. This peak is due to an increase in the density of states near the $\{111\}$ face due to the rigid band model predicting that the Fermi surface is beginning to lose contact with this face. Thus the discontinuity in the experimental curve for C_{44} is probably also due to a peak in the density of states near the $\{111\}$ face.

To analyze this correlation further, a departure from the rigid band model will now be made. Let all the basic assumptions of the rigid band model hold; and, consider the effect of the presence of the solute on the block states of the conduction electrons. The presence of the solute no longer makes the lattice perfectly periodic such that the block states are no longer rigorously valid eigen states.^{20,21} This has the effect of lessening the influence of the Brillouin zone on the conduction electrons. The electrons become more like free electrons which makes the Fermi surface become more spherical. This will obviously have a large effect on the area of contact at the $\{111\}$ faces; and only a small effect on the Fermi surface near the $\{200\}$ faces since this portion of the Fermi

surface is fairly spherical. This effect will therefore alter the density of states near the $\{111\}$ faces in a manner which is dependent on n in addition to the q dependence of the density of states predicted by the rigid band model.

The experimental results of the measurements of the electronic contribution to the specific heat of copper-nickel and copper-zinc alloys offers qualitative support for this spherification model. For the copper-zinc alloys, the density of states determined from the electronic specific heat measurements¹⁸ increases with q ; whereas, the rigid band model predicts a decrease. This can be interpreted as the area of contact with the $\{111\}$ faces not increasing with q as rapidly as the rigid band model predicts due to a spherification of the Fermi surface. Similarly, the density of states determined from the electronic specific heat measurements of the copper-nickel alloys⁵⁴ increases more rapidly with decreasing q than predicted by the rigid band model. This can also be interpreted in terms of the area of contact decreasing more rapidly with q due to this spherification of the Fermi surface. The results of this spherification will therefore result in a slope discontinuity in the density of states curve at $q = 1.0$ which is due primarily to the density of states associated with the Fermi surface near the $\{111\}$ face.

The effects of the spherification model can be incorporated into Collins' calculation through the band gaps. The band gaps determine the departure from sphericity of the Fermi surface. For example, a smaller band gap will result in less distortion of the Fermi surface. The spherification model then predicts that the

band gaps will decrease with increasing solute concentration. Collins also calculated the dependence of the electronic contribution to the shear constants on q for lower band gaps. As the band gaps become lower, the slope discontinuity in the curve for C_{44} occurs at higher q values. For example, a crude extrapolation of Collins' curves indicates that gaps only 10 per cent lower than the gaps needed to fit the Fermi surface data of pure copper will place the slope discontinuity near $q = 1.0$. The variation of C' with q remains the same for reasonable band gaps; but, the magnitude of the variation of both C' and C_{44} is greatly reduced as the band gaps are lowered. The magnitude of these band gaps also determines the amount the Fermi surface is altered from a shear deformation of the Brillouin zone and consequently the magnitude of this contribution to the shear constants. Since the dependence of the band gaps on solute concentration is not known, it is difficult to determine what the precise effect of the band gaps' dependence on solute concentration will be on the variation of C_{44} with q .

In light of the heat capacity measurements, it can be said that the density of states predicted by the rigid band model is not valid for the region of the Fermi surface near the $\{111\}$ faces. From these measurements it also appears that there is a slope discontinuity in the density of states associated with this region at $q = 1.0$. Since a slope discontinuity in the density of states near the $\{111\}$ faces in Collins' calculation also leads to a slope discontinuity in the curve of the dependence of C_{44} on q , there is reason to suspect that this may be the cause of the observed

slope discontinuity at $q = 1.0$. Further evidence for this is that spherification produces a larger density of states near the $\{111\}$ face than predicted by the rigid band model. The effect of this will be to decrease the magnitude of increase of C_{44} with increasing q for values of q greater than one; and, the observed increase is less than the predictions of Collins. The fair agreement with C' exhibits some support for this spherification model since the Fermi surface near the $\{200\}$ faces is not drastically affected by this spherification; and, one would expect the rigid band model to be an adequate approximation to the dependence of C' on q .

In order to obtain a more complete picture of this system, the bulk modulus will now be examined. The dependence of the normalized 0°K bulk modulus on the change in molar volume, ΔV , upon alloying is shown in Figure 24. The bulk modulus is linear in molar volume which is different from the behavior of the shear constants which are linear in q . The dependence of the isochoric bulk modulus on q is shown in Figure 25. The isochoric bulk modulus increases linearly with q for both alloy systems; but, there is a slope discontinuity in this plot at $q = 1.0$. The rate of increase of the isochoric bulk modulus with q for the copper-zinc alloys is approximately 2.0 times the rate of increase with q for the copper-nickel alloys. It is interesting to note that the rate of increase of the molar volume at room pressure with q for the copper-zinc alloys is also 2.0 times the rate of increase with q for the copper-nickel alloys.

Since a theoretical calculation of the bulk modulus is more

FIGURE 24. The normalized isobaric bulk modulus, $B(P=0)$, as a function of the change in molar volume due to alloying for the copper-nickel alloys and the copper-zinc alloys.

FIGURE 25. The normalized isochoric bulk modulus, $B(V')$, as a function of the electron per atom ratio for the copper-nickel alloys and the copper-zinc alloys.

complex than that of the shear constants, a very simple model will be employed in order to gain some feel for the relative magnitude of the dependence of the contribution from the band structure to the bulk modulus on q . It will be assumed that the only term in the band structure which is affected by the addition of the solute is the average Fermi energy of the conduction electrons and that this average Fermi energy can be represented by a free electron gas. This variation of the bulk modulus with q for a free electron gas is also shown by the dashed line in Figure 24. This contribution increases with q and comes very close to representing the experimental results for the copper-zinc alloys. Since the change in the average Fermi energy should be the dominant contribution to the variation of the bulk modulus with q , it appears that the variation of the bulk modulus with q can be interpreted from the band structure contributions which was what was done for the shear constants. It should be noted that an attempt to explain the variation of the bulk modulus with q for the copper-zinc alloys with this simple model is not being made. Only the relative magnitude of this model with q should be considered; and, the agreement of this model with the experimental results for the copper-zinc alloys should be considered as being more or less coincidental.

The slope discontinuity of the isochoric bulk modulus at $q = 1.0$ is still puzzling. Various experimental properties of the copper-nickel alloy system tend to indicate that the effective valency of nickel in copper is not zero even for small nickel concentrations. The results of photoemission and reflectivity measure-

ments of Seib and Spicer⁵⁵ indicate that the copper 3d states and the Fermi level do not change appreciably with nickel concentration; but, the addition of nickel produces an increase in the number of states between the top of the copper 3d band and the Fermi level. This means that the rigid band model may not be applicable to this system; and, Friedel's⁵⁶ virtual-bound-state model may best describe this system. This may be further substantiated by the fact that the density of states determined from magnetic susceptibility measurements as shown by Pugh and Ryan⁵⁷ is anomalously high; but, this density of states is also much higher than the density of states determined from specific heat measurements. This tends to indicate the presence of a nearly filled 3d band; but, the measurements are complicated by the possible existence of small ferromagnetic clusters of pure nickel which interact with the conduction electrons as well as contribute to the susceptibility. This is supported by the specific heat measurements of Gupta, Cheng, and Beck⁵⁴ and the susceptibility measurements of Ryan, Pugh, and Smoluchowski⁵⁸. Although these clusters may account for some of this anomalous behavior, the hypothesis is usually made that the nickel 3d band is not completely filled and contributes a fraction of an electron per atom to the conduction band.

If this is the case, the nickel 3d band will be nearly filled and be very narrow. Consequently, it will have a low degeneracy temperature. This is very similar to the d band of palladium. Rayne⁵⁹ measured the variation of the shear constants of palladium with temperature; and, the results of his measurements show an

anomalous temperature dependence. As the temperature increases above 20°K the shear constants begin to decrease linearly with temperature as is the case with most materials. At a temperature of 100°K the shear constant C_{44} begins to increase with temperature while the shear constant C' begins to decrease with increasing temperature at a progressively slower rate. Rayne successfully accounted for this anomalous temperature dependence with a model consisting of a nearly filled parabolic d band which was very narrow thereby resulting in a low degeneracy temperature. If this is the case for the copper-nickel alloys, then the shear constants should also exhibit this anomalous temperature dependence; however, the temperature dependence of both the isochoric and isobaric shear constants of the alloys is identical to that of pure copper. Rayne also showed that the contribution to the bulk modulus from a nearly filled d band is also fairly large. If this is the case for the copper-nickel alloys, then one might expect the isochoric bulk modulus to increase with solute concentration; but, the isochoric bulk modulus actually decreases. Therefore, the experimental results of the elastic constants of the copper-nickel alloys indicates that a narrow nearly filled d band may not exist.

This slope discontinuity may then be due to the assumption that the ion-ion repulsive interaction is unaffected by the addition of the solute. Since the nickel d band may not form a common d band with copper, one might expect the short range ion-ion interaction to vary with solute concentration. Since it is difficult to interpret the contribution to the elastic constants from the short

range ion-ion interaction by using this band model, let us consider a case where there is definitely a change in the short range interaction. Silver and gold have lattice parameters differing by less than 0.1% such that their molar volumes are approximately the same; and, their band structure is fairly similar. Daniels and Smith⁶ measured both the elastic constants and their pressure derivatives for these metals and showed that there is an appreciable difference in the short range ion-ion interaction. If a comparison of the elastic constants and their pressure derivatives of these two metals is made, one can see large differences in some of the elastic constants and their pressure derivatives. Since no large differences in the elastic constants and their pressure derivatives were observed for the copper-nickel alloys, the assumption that the short range ion-ion interaction is unaffected by the addition of the solute appears reasonable.

This slope discontinuity is difficult to explain due to the many variables and approximations used to calculate the bulk modulus. It could be due to the band gaps being a function of solute concentration or to the charging effects which Stern^{20,21} has used successfully to explain some of the anomalies of the noble metal alloys; but, too little is actually known about the volume dependence of the internal energy and its variation with solute concentration to even make a definite qualitative estimate.

CONCLUSIONS

Many models are used to explain the physical properties of the noble metals and the noble metal alloys; but, there is no single model which gives a satisfactory explanation of the experimental results. The main difficulty arises in determining the change in the Fermi surface upon alloying and in determining just what the configuration of the d electrons is for these alloys. These measurements were made in order to completely specify the elastic properties of this alloy system at constant volume. Since the theorist made their calculations at constant volume, it is hoped that this may be helpful to them in their difficult task of explaining the physical properties of these alloys.

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