

① Elast. Constants
 ② Nickel
 ③ Copper EPST SG65 0173

THE ELASTIC CONSTANTS OF NICKEL-COPPER ALLOY SINGLE CRYSTALS*

S. G. EPSTEIN† and O. N. CARLSON‡

The elastic constants of single crystals of the nickel-copper alloy system were determined by an ultrasonic pulse-echo technique. The elastic constants are proportional to the nickel concentration up to 70 at. % nickel at room temperature. Above this concentration where the alloys are ferromagnetic at ambient temperatures a slight positive deviation from linearity is observed in the elastic constant versus composition curves. The ΔE -effect was observed in all of the ferromagnetic nickel-rich alloys.

LES CONSTANTES ELASTIQUES DE MONOCRISTAUX D'ALLIAGES NICKEL-CUIVRE

Les auteurs ont déterminé les constantes élastiques de monocristaux d'alliages du système nickel-cuivre, en utilisant la technique de l'impulsion ultrasonore et de l'écho. Les constantes élastiques sont proportionnelles à la teneur en nickel jusqu'à 70% at., à la température ambiante. Au-dessus de cette concentration, pour laquelle les alliages sont ferromagnétiques à la température ambiante, on observe une légère déviation positive par rapport à la loi linéaire dans les courbes constante élastique-composition. L'effet ΔE a été observé dans les alliages riches en nickel et ferromagnétiques.

DIE ELASTISCHEN KONSTANTEN VON EINKRISTALLEN DER NICKEL-KUPFER-LEGIERUNGEN

Die elastischen Konstanten von Einkristallen des Legierungssystem Nickel-Kupfer wurden mit einer Puls-Echo Ultraschallmethode bestimmt. Die elastischen Konstanten sind bei Raumtemperatur proportional zur Nickelkonzentration bis herauf zu 70 At.-% Nickel. Oberhalb dieser Konzentration, wo die Legierungen bei Raumtemperatur ferromagnetisch sind, beobachtet man bei der Auftragung der elastischen Konstanten gegen die Zusammensetzung eine leichte positive Abweichung von der Linearität. Der ΔE -Effekt wurde in allen ferromagnetischen nickelreichen Legierungen beobachtet.

INTRODUCTION

While elastic constants have been measured for many pure metals, there exists a scarcity of data in the scientific literature on alloy single crystals.⁽¹⁾ At the time this study was undertaken, the authors were aware of no reported complete sets of elastic constants obtained for single crystals with compositions encompassing an entire alloy system.

The elastic constants of copper single crystals have been measured by Goens⁽²⁾ by a composite oscillator technique and by Lazarus,⁽³⁾ Overton and Gaffney,⁽⁴⁾ and Schmunk and Smith,⁽⁵⁾ all of whom used an ultrasonic pulse-echo method. The elastic constants of nickel single crystals have been measured by Honda and Shirakawa,⁽⁶⁾ Yamamoto,⁽⁷⁾ Bozorth *et al.*,⁽⁸⁾ Neighbours *et al.*,⁽⁹⁾ Levy and Truell,⁽¹⁰⁾ de Klerk and Musgrave,⁽¹¹⁾ and Alers *et al.*⁽¹²⁾ employing various techniques. There is generally good agreement in the results of these investigations for copper but

the nickel values show considerable differences. This is probably due, at least in part, to the different techniques employed and to variations in the domain distributions in unmagnetized nickel crystals.⁽⁸⁾

Previous to this investigation Shirakawa and Numakura,⁽¹³⁾ determined Young's moduli for the principal crystallographic orientations in nickel-copper alloy single crystals and Schmunk and Smith studied the effects of small additions of nickel on some of the elastic constants of copper using the pulse-echo technique. Very recently Sakurai *et al.*⁽¹⁴⁾ published results of their study of the elastic constants of Ni-Fe and Ni-Cu alloys over a wide composition range. They incorporated the data of the above mentioned investigations in their treatment of the Ni-Cu case from which they observed a linear variation in elastic constants with composition. These results were interpreted in terms of the central and pair-like interactions between atoms. The present study attempts to provide a complete description of the dependence of the room temperature elastic constants on composition across the nickel-copper alloy system.

EXPERIMENTAL PROCEDURES

Single crystals of nickel and copper and of Ni-Cu alloys in the composition range of 6 to 84 at. % Cu

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† Institute for Atomic Research, Iowa State University, Ames, Iowa and Brookhaven National Laboratory, Upton, New York.

‡ Institute for Atomic Research and Department of Metallurgy, Iowa State University, Ames Iowa.

were grown by a modified Bridgman technique. The materials used in this investigation were high purity copper of 99.9 per cent purity and nickel pellets of 99.95 per cent purity with iron as the major impurity. The furnace core consisted of a graphite resistor tube with a reduced cross-section which produced a sharp temperature gradient in the furnace. The specimen was contained in a ceramic crucible with a conically-shaped bottom which was supported within the furnace

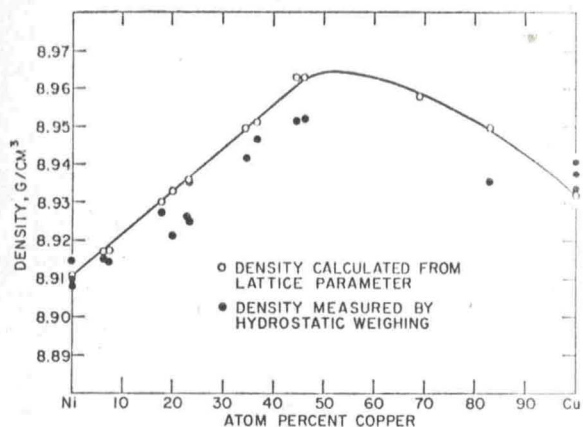


Fig. 1. Theoretical and measured densities of nickel-copper alloy single crystals.

by a tantalum rod connected to a positioning arm by means of which the crucible was raised and lowered through the temperature gradient. Graphite crucibles were used for the pure copper crystals, while BeO crucibles were utilized for nickel and all of the alloy crystals. A more detailed description of the apparatus and the technique employed for growing these crystals is given in a report by Armstrong and Carlson.⁽¹⁵⁾

Single crystals approximately 3 cm in diameter and 2.5 cm in length, exclusive of the conical bottom section, were obtained for all compositions. Their orientations were determined by a Laue back-reflection X-ray technique and plates were cut with faces oriented for either the [100] or [110] crystallographic direction. Plates intended for pulse-echo measurements were cut to a thickness of from 0.5 to 2 cm while those for resonance measurements were less than 0.25 cm thick. All the plates were carefully hand lapped and polished, to produce faces deviating less than 0.001 cm from parallelism and aligned to within 2 degrees of the desired crystallographic axis.

Chemical analysis of samples taken from upper and lower regions of the ingots revealed no detectable concentration gradients; however, in most instances the actual composition was from 2 to 4 per cent off from the intended composition due to the vaporization of copper.

Alloys containing up to 30 at.% Cu were observed

to exhibit ferromagnetic behavior at room temperature. Curie temperatures determined for pure nickel and the nickel-rich alloys were in good agreement with values reported by Krupkowski⁽¹⁶⁾ and Marian.⁽¹⁷⁾ In the as-grown condition these alloys showed a rather sluggish transition from the ferromagnetic to paramagnetic states probably due to coring or micro-segregation. However, after annealing for 200 hr at approximately 1100°C in a helium atmosphere these same specimens exhibited a sharp transition temperature.

The lattice parameter was determined for each alloy from X-ray powder patterns and its density was calculated therefrom. A comparison of the alloy densities thus determined with those obtained by hydrostatic weighing is given in Fig. 1. These data are in good agreement with those obtained from lattice parameter values reported by Coles⁽¹⁸⁾ for Ni-Cu alloys particularly at the nickel-rich end of the system. The calculated density represented by the data points in the figure was used in the elastic constant calculations.

The adiabatic elastic constants were determined from ultrasonic velocities measured by the pulse-echo method. The basic apparatus and techniques employed in this investigation are described in a previous Ames Laboratory report.⁽¹⁵⁾ An important modification of this apparatus was the substitution of a Tektronix type 545 oscilloscope with a self-contained sweep delay for the original external sweep-delay to measure elapsed time between the echos generated by the 10 megacycle pulse. Quartz piezoelectric transducers, $\frac{1}{2}$ in. square and gold-plated on one face, were acoustically bonded to the single crystalline plates with phenyl salicylate (salol).

Transit times for the ultrasonic signals were measured for each specimen from echoes of the pulse at temperatures between -40 and 40°C. This experimental work was performed before Eros and Reitz⁽¹⁹⁾ had published their experiments on elimination of the transit time error, hence a correction for the errors in transit time associated with the partial reflection and transmission of the ultrasonic pulse at the crystal-quartz interface was applied to the calculation of the elastic constants. The magnitude of this time delay was determined for longitudinal wave propagation by comparing the velocities obtained by the pulse-echo method with velocities measured by a resonant-frequency technique described by Bhagavantam and Bhimasenachar.⁽²⁰⁾ Since the latter method is only applicable to longitudinal vibrations, the transit time delay encountered with shear waves was determined by the measurement of transit times in plates of

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Compo-
sition
at. % Cu

Ni
Ni
7.3
17.8
22.8
34.5
34.5
46.2
68.9
Cu
Cu

TABLE 1. Elastic constants measured by pulse echo method in Ni-Cu alloy plates with [100] orientation

Composition at. % Cu	Plate thickness cm	$C_{11} \times 10^{-12}$ dyn/cm ²		$C_{44} \times 10^{-12}$ dyn/cm ²		
		Magnetically saturated	Unmagnetized	Unmagnetized plates by reso- nance method ^a	Magnetically saturated	Unmagnetized
Ni	0.69	2.504	2.481	2.478	1.258	1.244
6.4	0.64	2.449	2.421	2.395	1.223	1.209
20.1	1.61	2.298	2.294		1.132	1.130
23.1	0.62	2.291	2.280	2.280	1.131	1.125
36.6	0.64		2.144	2.156		1.064
36.6	1.26	2.145	2.138			1.057
83.8	1.88		1.800			0.825
Cu	0.74		1.697	1.683		0.753

Notes:

^a For comparison with pulse-echo results; specimen thickness approximately 0.25 cm.

varying thicknesses cut from the same crystal. The transit time delays found by these procedures were 0.02 μ -sec for longitudinal waves and 0.04 μ -sec for shear wave propagation. Measurements on pure nickel and alloys containing up to 40 at. % Cu were made by the pulse-echo technique in both the magnetically saturated and unmagnetized conditions. All of the resonance measurements were taken on unmagnetized specimens.

EXPERIMENTAL RESULTS

The ultrasonic transit time for each crystal was established at 25°C from transit time *versus* temperature curves constructed from the pulse-echo data. After applying the appropriate transit time corrections, velocities of wave propagation were determined. The elastic constants, C_{ij} , were calculated from the velocity v and the density ρ according to the relationships given below. For wave propagation in the [100] crystallographic direction:

$$\rho v_1^2 = C_{11} \text{ for a longitudinal wave,}$$

$$\rho v_2^2 = C_{44} \text{ for a transverse wave polarized in any direction in the [100] plane.}$$

For wave propagation in the [110] crystallographic direction:

$$\rho v_3^2 = C_L' = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}) \text{ for a longitudinal wave,}$$

$$\rho v_4^2 = C_{44} \text{ for a transverse wave polarized in the [001] direction,}$$

$$\rho v_5^2 = C' = \frac{1}{2}(C_{11} - C_{12}) \text{ for a transverse wave polarized in the [110] direction.}$$

The adiabatic elastic constants obtained by the pulse-echo and resonance techniques are presented in Tables 1 and 2. The application of a magnetic field to the nickel-rich specimens resulted in an increase of about 1 per cent in the elastic constants, and a marked diminution in the attenuation of the ultrasonic vibrations. As Levy and Truett⁽¹⁰⁾ have shown, the shear modes induce much greater acoustic losses in nickel than the longitudinal modes. The rate of attenuation was so great that only one echo could be detected with the shear wave polarized in the [110] direction in the nickel-rich alloys in the unmagnetized condition. This prevented our obtaining a reliable

TABLE 2. Elastic constants measured by pulse echo method in Ni-Cu plates with [110] orientation

Compo- sition at. % Cu	Plate thick- ness cm	$C_L' \times 10^{-12}$ dyn/cm ²			$C_{44} \times 10^{-12}$ dyn/cm ²		$C' \times 10^{-12}$ dyn/cm ²	
		Magnetically saturated	Unmagnet- ized	Unmagnetized plates by resonance method	Magnet- ically saturated	Unmagnet- ized	Magnetically saturated	Unmagnet- ized
Ni	0.65	3.298	3.255	3.226	1.254	1.241	0.489	too much attenuation
Ni	1.80	3.272	3.259		1.247	1.243	0.486	too much attenuation
7.3	0.61	3.210	3.163		1.217	1.201	0.454	too much attenuation
17.8	0.56	3.079	3.041	3.030	1.159	1.146	0.407	too much attenuation
22.8	0.55	3.010	2.990	2.995	1.125	1.113	0.385	too much attenuation
34.5	0.56		2.879			1.062		0.352
34.5	1.19		2.875			1.061		0.353
46.2	0.77		2.766	2.767		1.009	Non-magnetic	0.329
68.9	1.20		2.501			0.896	Non-magnetic	0.286
Cu	0.70		2.204	2.213		0.760	Non-magnetic	0.236
Cu	1.87		2.205			0.754	Non-magnetic	0.235

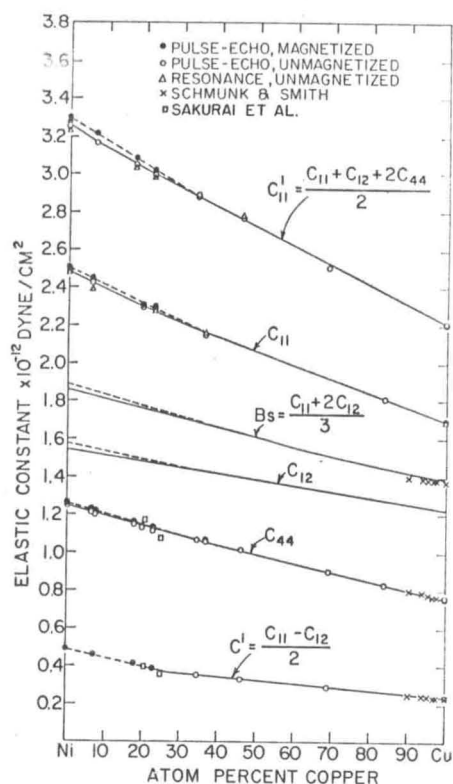


FIG. 2. The elastic constants of nickel-copper alloy single crystals in the magnetically saturated and unmagnetized states.

velocity determination in this case but in the magnetically saturated condition enough echoes were generated to permit an accurate determination (see column C of Table 2). No difference in the velocity or in the attenuation of the ultrasonic waves could be detected between measurements taken with the magnetic field parallel to the crystal axis and with the field perpendicular to the axis. The absence of any significant effects of field direction would be expected considering the low magnetostriction of nickel.

The data from Tables 1 and 2 are plotted in Fig. 2 showing graphically the relationship between the measured constants C_{11} , C_{44} , C' and C_L' , and alloy composition. The C_{12} curve was derived from these data using the equation $C_{12} = 2C_L' - C_{11} - 2C_{44}$. The bulk modulus, B_s , was derived in a similar manner. The C_{12} constant was also determined from the relationship, $C_{12} = C_{11} - 2C'$ with good agreement being obtained in the two cases. The data of Schmunk and Smith⁽⁵⁾ for the composition range of 0-10 at.% Ni were included in the construction of these curves as were the experimental points of Sakurai and co-workers.⁽¹⁴⁾

The dashed lines of Fig. 2 represent data for alloys in the magnetically saturated state. Although the

increase in the elastic constants produced by application of the magnetic field is quite small, approaching the limit of experimental reliability in some cases, the difference is real and measurable. Repeated measurements made on individual specimens in the as-prepared condition, after magnetization and after annealing above the Curie temperature to demagnetize them gave reproducible evidence for this difference.

DISCUSSION

The elastic constants of pure copper obtained in this investigation are in good agreement with those reported by others and the elastic constants for both unmagnetized and magnetically saturated nickel single crystals also fall within the range of values reported in the literature. The addition of nickel to copper results in a linear increase in all of the elastic constants of copper over the composition range of 0 to 70 at.% Ni. The slopes of these lines can be expressed as the quantity $(1/C_0)(dC/dx)$ where C_0 is the corresponding constant for pure copper and dC/dx is the change in this constant with composition. This value for C_{44} is 0.61 and for C' is 0.74 as compared with Schmunk and Smith's values of 0.57 and 0.70 respectively which they obtained for dilute alloys of nickel in copper. Thus the linear relationship that Schmunk and Smith observed in the shear constants in the dilute solid solution range holds across most of the system. The unmagnetized alloys exhibit a slight deviation from this linearity in the ferromagnetic composition range for all but the derived C_{12} curve which is linear across the entire system.

These results support the conclusion of Sakurai *et al.* of a linear elastic constant versus composition curve for this system and a zero or slightly positive dissociation energy. Inasmuch as they found it necessary to apply a correction factor to the data of Shirakawa and Numakura, the results of the present investigation provide stronger supporting evidence for this conclusion.

The increase in all of the elastic constants of the ferromagnetic alloys of this system upon magnetization, referred to as the ΔE -effect, has been observed previously in other ferromagnetic materials. This has been attributed to the orientation of the domain walls by magnetization, although it should also be pointed out that a difference in the transit time correction between the magnetically ordered and disordered states could also produce this effect. The values that were obtained for C_{11} and C_{44} on pure nickel in the magnetically saturated condition were about 1 per cent greater than in the unmagnetized state. Bozorth *et al.*⁽⁸⁾ and de Klerk and Musgrave⁽¹¹⁾

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report this same 1 per cent difference in C_{11} but a 3 to 4 per cent increase in C_{44} . They also found a slight decrease in the C_{12} value of pure nickel upon magnetization whereas the results of this work indicate a significant increase. Alloying with copper appears to reduce the magnitude of this ΔE effect in nickel as is shown by the convergence of the magnetized and unmagnetized curves at the boundary of the ferromagnetic region.

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REFERENCES

1. H. B. HUNTINGTON, *Solid State Physics* **7**, 213 (1958).
2. E. GOENS, *Physik. Z.* **37**, 321 (1936).
3. D. LAZARUS, *Phys. Rev.* **76**, 545 (1949).
4. W. C. OVERTON and J. GAFFNEY, *Phys. Rev.* **98**, 969 (1955).
5. R. E. SCHMUNK and C. S. SMITH, *Acta Met.* **8**, 396 (1960).
6. K. HONDA and Y. SHIRAKAWA, *Trans. Japan Inst. Metals* **1**, 217 (1937).
7. M. YAMAMOTO, *Phys. Rev.* **77**, 566 (1950).
8. R. M. BOZORTH, W. P. MASON and H. J. MCSKIMIN, *Bell System Tech. J.* **30**, 970 (1951).
9. J. R. NEIGHBOURS, F. W. BRATTEN and C. S. SMITH, *J. Appl. Phys.* **23**, 389 (1952).
10. S. LEVY and R. TRUPELL, *Rev. Mod. Phys.* **25**, 140 (1953).
11. J. DEKLERK and M. J. P. MUSGRAVE, *Proc. Phys. Soc. Lond.* **68B**, 81 (1955).
12. G. A. ALERS, J. R. NEIGHBOURS and H. SATO, *J. Phys. Chem. Solids* **13**, 40 (1960).
13. Y. SHIRAKAWA and K. NUMAKURA, *Sci. Rept. Res. Inst. Tohoku Univ.* **A10**, 51 (1958).
14. J. SAKURAI, M. FUJII, Y. NAKAMURA and H. TAKAKI, *J. Phys. Soc. Japan* **19**, 308 (1964).
15. P. E. ARMSTRONG and O. N. CARLSON, U.S.A.E.C. Rept. No. ISC-993 (1957).
16. A. KRUPKOWSKI, *Rev. Met. Memories* **26**, 131 (1920).
17. V. MARIAN, *Ann. Phys.* **7**, 459 (1937).
18. B. R. COLES, *J. Inst. Met.* **84**, 346 (1956).
19. S. EROS and J. R. REITZ, *J. Appl. Phys.* **29**, 683 (1958).
20. S. BHAGAVANTAM and J. BHIMASENACHAR, *Proc. Indian Acad. Sci.* **20**, 298 (1944).